

PROCEEDINGS  
OF THE  
NATIONAL ACADEMY OF SCIENCES  
INDIA  
1962

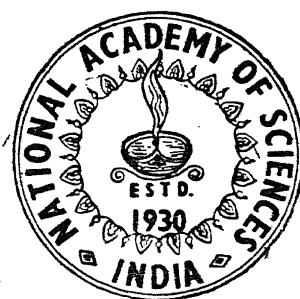
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Vol. XXXII

SECTION - A

Part IV

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ALLAHABAD

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VOL. XXXII

SECTION - A

PART IV

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ON THE DETERMINATION OF JUMP OF A FUNCTION  
BY ITS FOURIER COEFFICIENTS

By

SARLA SHARMA

*Department of Mathematics, Allahabad University, Allahabad*

[Received on 10th October, 1961]

1. Let  $f(x)$  be integrable L in the interval  $(-\pi, \pi)$  and have period  $2\pi$  and let its Fourier series be

$$f(x) = \frac{1}{2} a_0 + \sum_{v=1}^{\infty} (a_v \cos vx + b_v \sin vx) \quad (1.1)$$

Then the Conjugate series of (1.1) is

$$\sum_{n=1}^{\infty} (b_n \cos vx - a_n \sin vx) = \sum_{n=1}^{\infty} B_n$$

We write

$$\psi(t) = f(x+t) - f(x-t)$$

and

$$\psi^*(t) = f(x+t) - f(x-t) - D(x)$$

If  $\psi^*(t) \rightarrow 0$ , as  $t \rightarrow 0$ , then we have  $D \equiv D(x) = f(x+0) - f(x-0)$ , that is to say that  $D$  is the jump of a function at  $t = x$ . If  $\psi^*(t) \rightarrow 0$ , but satisfies some other condition, then  $D$  is said to be the generalized jump of the function at  $t = x$ .

We also write

$$\Psi_1^*(t) = \int_t^\pi \frac{|\psi^*(u)|}{u} du$$

*Definition* :—Let  $\sum a_n$  be a given infinite series and let  $\{\lambda_n\}$  be a positive monotonic increasing sequence which tends to infinity with  $n$ . Then the  $(R, \lambda_n, k)$  mean of the series  $\sum a_n$  is given by

$$C_\lambda^k(\omega) = \sum_{\lambda_n < \omega} \left(1 - \frac{\lambda_n}{\omega}\right)^k a_n$$

If we take  $\lambda(\omega)$  to be a monotonic increasing function of  $\omega$  in  $(0, \infty)$ , such that  $\lambda(\omega)$  tends to infinity with  $\omega$ , and if we write  $\lambda_n$  for  $\lambda(n)$ , then it is easy to see that

$$C_\lambda^k \left\{ \lambda(\omega) \right\} = \sum_{n < \omega} \left(1 - \frac{\lambda(n)}{\lambda(\omega)}\right)^k a_n.$$

2. For the determination of the generalized jump  $D(x)$  by the corresponding Fourier Coefficients Szász gave the following theorem :—

*Theorem 1.* If there exists a number  $D \equiv D(x)$  such that

$$\int_0^t \psi^*(u) du = o(t)$$

and

$$\int_0^t |\psi^*(u)| du = O(t)$$

as  $t \rightarrow 0$ , the  $\lim_{n \rightarrow \infty} \left\{ \bar{S}'_{2n}(x) - \bar{S}'_n(x) \right\} = \frac{\log 2}{\pi} D(x)$ . Where  $\bar{S}'_n(x)$

denotes the  $n$ th arithmetic mean of the sequence of partial sums of the conjugate series.

Making use of the  $(R, \log n, 1)$  mean of the series  $\sum B_n$  instead of the arithmetic mean of the sequence of its partial sums, M. L. Misra proved the theorem given below.

*Theorem 2.* If

$$\int_t^\pi \frac{|\psi^*(u)|}{u} du = o(\log^{-1} t)$$

as  $t \rightarrow 0$ , then  $\lim_{\omega \rightarrow \infty} (\bar{R}_1(2\omega) - \bar{R}_1(\omega)) = \frac{\log 2}{2\pi} D(x)$ , where  $\bar{R}_1(\omega) =$

$C_\lambda(\log \omega)$  and  $a_n = B_n(x)$ .

In the present paper we take another type of Riesz mean and establish the following theorem :—

**Theorem :**

If there exists a number  $D \equiv D(x)$  such that, for  $\Delta < 1$

$$\Psi_1^*(t) = \int_0^{\pi} \frac{|\psi^*(u)|}{u} du = O((\log^{1/t} \Delta)),$$

as  $t \rightarrow 0$ , then  $\lim_{\omega \rightarrow \infty} (\sigma_1(2\omega) - \sigma_1(\omega)) = \frac{\log 2}{\pi} D(x)$ , where  $\sigma_1(\omega) = C_{\lambda} \left\{ \lambda(\omega) \right\}$ ,

$a_n = B_n(x)$  and  $\lambda(\omega) = \begin{cases} 0, 1 \leq \omega < e^2 \\ \frac{e(\omega)}{\omega}, \omega > e^2, \end{cases} \delta > 1$  and  $e(\omega) = e^{(\log \log \omega)^{\delta}}$ .

3. We require the following lemmas :—

**Lemma 1.** Let  $\sigma_k(\omega) = C_{\lambda}^k \left\{ \lambda(\omega) \right\}$ , where  $\lambda(\omega)$  define as in the above theorem.

Then

$$\sigma_k'(\omega) = \frac{K \delta (\log \log \omega)^{\delta-1}}{\omega \log \omega} [ \sigma_{k-1}(\omega) - \sigma_k(\omega) ].$$

**Proof of the Lemma 1.** We have

$$\begin{aligned} \sigma_k'(\omega) &= \frac{d}{d\omega} \left[ \sum_{e^2 \leq n \leq \omega} \left( 1 - \frac{e(n)}{e(\omega)} \right)^k C_n + \sum_{1 \leq n < e^2} C_n \right] \\ &= \sum_{e^2 \leq n \leq \omega} \left( 1 - \frac{e(n)^{k-1}}{e(\omega)} \right) \frac{K \delta e(n) (\log \log \omega)^{\delta-1}}{e(\omega) \omega \log \omega} C_n \\ &= \frac{K \delta (\log \log \omega)^{\delta-1}}{\omega \log \omega} \sum_{e^2 \leq n \leq \omega} \left[ \left( 1 - \frac{e(n)}{e(\omega)} \right)^{K-1} - \left( 1 - \frac{e(n)}{e(\omega)} \right)^K \right] C_n \\ &= \frac{K \delta (\log \log \omega)^{\delta-1}}{\omega \log \omega} ( \sigma_{k-1}(\omega) - \sigma_k(\omega) ) \end{aligned}$$

**Lemma 2.**

As  $\omega \rightarrow \infty$ ,

$$(i) \int_{e^2}^{\omega} \frac{e(x)}{x} dx = \frac{e(\omega) \log \omega}{\delta (\log \log \omega)^{\delta-1}} + O\left(\frac{e(\omega) \log \omega}{(\log \log \omega)^{2(\delta-1)}}\right)$$

and

$$(ii) \int_{\omega}^{\infty} \frac{1}{x(\log \log x)^{\delta-1}} dx = o(1)$$

where  $\delta > 1$ .

Proof of the Lemma 2 (i). Integrating by parts, we obtain

$$\begin{aligned} \int_{\omega}^{\infty} \frac{\varepsilon(x)}{x} dx &= \int_{\omega}^{\infty} \frac{\varepsilon(x) \delta (\log \log x)^{\delta-1}}{x \log x} \frac{\log x}{\delta (\log \log x)^{\delta-1}} dx \\ &= \left[ \frac{\varepsilon(x) \log x}{\delta (\log \log x)^{\delta-1}} \right]_{\omega}^{\infty} - \int_{\omega}^{\infty} \frac{\varepsilon(x)}{x \delta} \left[ \frac{\log \log x - (\delta-1)}{(\log \log x)^{\delta}} \right] dx \\ &= \frac{\varepsilon(\omega) \log \omega}{\delta (\log \log \omega)^{\delta-1}} + O\left(\frac{\varepsilon(\omega) \log \omega}{(\log \log \omega)^{2(\delta-1)}}\right) \end{aligned}$$

Proof of Lemma 2 (ii). We have for  $\delta > 1$ ,

$$\begin{aligned} \int_{\omega}^{2\omega} \frac{1}{x(\log \log x)^{\delta-1}} dx &< \frac{1}{(\log \log \omega)^{\delta-1}} \int_{\omega}^{2\omega} \frac{1}{x} dx \\ &= \frac{1}{(\log \log \omega)^{\delta-1}} \log 2 \end{aligned}$$

as  $\omega \rightarrow \infty$ ,

$$= o(1)$$

4. Proof of the Theorem. We have in the notation of Lemma 1.

$$\begin{aligned} \sigma_0(\omega) &= \sum_{n < \omega} B_n(x) = \frac{1}{2\pi} \int_0^{\pi} \left\{ f(x+t) - f(x-t) \right\} \text{Cot} \frac{t}{2} (1 - \text{Cos} \omega t) dt + o(1) \\ &= \frac{D}{2\pi} \int_0^{\pi} \text{Cot} \frac{t}{2} (1 - \text{Cos} \omega t) dt \\ &\quad + \frac{1}{2\pi} \int_0^{\pi} \psi^*(t) \text{Cot} \frac{t}{2} (1 - \text{Cos} \omega t) dt + o(1) \\ &= \frac{D}{\pi} \log(2\omega + \gamma) + \frac{1}{2\pi} \int_0^{\pi} \psi^*(t) \left( \text{Cot} \frac{t}{2} - \frac{2}{t} \right) (1 - \text{Cos} \omega t) dt \end{aligned}$$

$$+ \frac{1}{\pi} \int_0^\pi \psi^*(t) \frac{1 - \cos \omega t}{t} dt + o(1).$$

$$= \frac{D}{\pi} \log \omega + \frac{1}{\pi} \int_0^\pi \psi^*(t) \frac{1 - \cos \omega t}{t} dt + o(1)$$

Also

$$\begin{aligned} \bar{\sigma}_1(\omega) &= \sum_{\epsilon^2 \leq n \leq \omega} \left[ 1 - \frac{\epsilon(n)}{\epsilon(\omega)} \right] B_n + \sum_{1 \leq n < \epsilon^2} B_n \\ &= \frac{1}{\epsilon(\omega)} \int_{\epsilon^2}^\omega \left\{ \sum_{n < \omega} B_n - \sum_{1 \leq n < \epsilon^2} B_n \right\} \frac{\delta_{\epsilon}(x) (\log \log x)^{\delta-1}}{x \log x} dx + \sum_{1 \leq n < \epsilon^2} B_n \\ &= \frac{1}{\epsilon(\omega)} \int_{\epsilon^2}^\omega \bar{\sigma}_0(x) \cdot \frac{\delta_{\epsilon}(x) (\log \log x)^{\delta-1}}{x \log x} dx - \frac{\epsilon(\log 2)^\delta}{\epsilon(\omega)} \sum_{1 \leq n < \epsilon^2} B_n + O(1) \\ &= \frac{D}{\pi \epsilon(\omega)} \int_{\epsilon^2}^\omega \log x \cdot \frac{\delta_{\epsilon}(x) (\log \log x)^{\delta-1}}{x \log x} dx \\ &+ \frac{1}{\pi \epsilon(\omega)} \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{(1 - \cos xt)}{t} dt \frac{\delta_{\epsilon}(x) (\log \log x)^{\delta-1}}{x \log x} dx + O(1) \\ &= \frac{D}{\pi} \log \omega - \frac{D}{\pi \epsilon(\omega)} \int_{\epsilon^2}^\omega \frac{\epsilon(x)}{x} dx \\ &+ \frac{1}{\pi \epsilon(\omega)} \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{1 - \cos xt}{t} dt \frac{\delta_{\epsilon}(x) (\log \log x)^{\delta-1}}{x \log x} dx + O(1) \end{aligned}$$

Now by the Lemma 1.

$$\begin{aligned} \frac{d}{d\omega} \bar{\sigma}_1(\omega) &= \frac{\delta (\log \log \omega)^{\delta-1}}{\omega \log \omega} \left[ \bar{\sigma}_0(\omega) - \bar{\sigma}_1(\omega) \right] \\ &= C \left[ \bar{\sigma}_0(\omega) - \bar{\sigma}_1(\omega) \right] \end{aligned}$$

say. Hence

$$\frac{\pi}{\zeta} \frac{d}{d\omega} \sigma_1(\omega) = D \log \omega + \int_0^\pi \psi^*(t) \frac{(1 - \cos \omega t)}{t} dt + O(1)$$

$$= D \log \omega + \frac{D}{\epsilon(\omega)} \int_{\epsilon^2}^\omega \frac{\epsilon(x)}{x} dx + O(1)$$

$$= \frac{1}{\epsilon(\omega)} \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{(1 - \cos x t)}{t} dt \frac{\delta \epsilon(x) (\log \log x)^{\delta-1}}{x \log x} dx,$$

$$= \frac{D}{\epsilon(\omega)} \int_{\epsilon^2}^\omega \frac{\epsilon(x)}{x} dx + O(1)$$

$$+ \frac{1}{\epsilon(\omega)} \left\{ \begin{aligned} & \left( \epsilon(\omega) \int_0^\pi \psi^*(t) \frac{(1 - \cos \omega t)}{t} dt \right. \\ & \left. - \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{(1 - \cos x t)}{t} dt \frac{\delta \epsilon(x) (\log \log x)^{\delta-1}}{x \log x} dx \right) \end{aligned} \right\}$$

$$= \frac{D}{\epsilon(\omega)} \left\{ \frac{\epsilon(\omega) \log \omega}{\delta (\log \log \omega)^{\delta-1}} + O\left(\frac{\log \omega \cdot \epsilon(\omega)}{(\log \log \omega)^{2(\delta-1)}}\right) \right\} + O(1)$$

$$+ \frac{1}{\epsilon(\omega)} \left\{ \begin{aligned} & \left( \epsilon(\omega) \int_0^\pi \psi^*(t) \frac{(1 - \cos \omega t)}{t} dt \right. \\ & \left. - \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{(1 - \cos x t)}{t} dt \frac{\delta \epsilon(x) (\log \log x)^{\delta-1}}{x \log x} dx \right) \end{aligned} \right\}$$

by virtue of Lemma 2 (ii)

Now

$$\frac{1}{\epsilon(\omega)} \left\{ \begin{aligned} & \left( \epsilon(\omega) \int_0^\pi \psi^*(t) \frac{(1 - \cos \omega t)}{t} dt \right. \\ & \left. - \int_{\epsilon^2}^\omega \int_0^\pi \psi^*(t) \frac{(1 - \cos x t)}{t} dt \frac{\delta \epsilon(x) (\log \log x)^{\delta-1}}{x \log x} dx \right) \end{aligned} \right\}$$

$$\begin{aligned}
&= \frac{1}{\underline{\epsilon}(\omega)} \left\{ \begin{aligned}
&\underline{\epsilon}(\omega) \int_0^{\pi} \psi^*(t) \frac{(1 - \cos \omega t)}{t} dt \\
&- \int_0^{\pi} \psi^*(t) dt \left[ \frac{(1 - \cos \omega t)}{t} \underline{\epsilon}(\omega) \right] \frac{\omega}{\epsilon^2}
\end{aligned} \right\} \\
&+ \frac{1}{\underline{\epsilon}(\omega)} \int_0^{\pi} \psi^*(t) \int_{\epsilon^2}^{\omega} \sin x t \underline{\epsilon}(x) dx dt \\
&= \frac{\epsilon^{(\log 2)^\delta}}{\underline{\epsilon}(\omega)} \int_0^{\pi} \psi^*(t) \frac{(1 - \cos \epsilon^2 t)}{t} dt \\
&+ \frac{1}{\underline{\epsilon}(\omega)} \int_0^{\pi/\omega} |\psi^*(t)| O(\omega \underline{\epsilon}(\omega)) dt + \frac{1}{\underline{\epsilon}(\omega)} \int_{\pi/\omega}^{\pi} |\psi^*(t)| O\left(\frac{1}{t} \underline{\epsilon}(\omega)\right) dt \\
&< \frac{\epsilon^{(\log 2)^\delta}}{\underline{\epsilon}(\omega)} \left[ \int_0^{\pi/\omega} |\psi^*(t)| - \frac{\epsilon^4 t}{2} dt + \int_{\pi/\omega}^{\pi} \frac{|\psi^*(t)|}{t} dt \right] \\
&+ O(\omega) \int_0^{\pi/\omega} |\psi^*(t)| dt + O(1) \int_{\pi/\omega}^{\pi} \frac{|\psi^*(t)|}{t} dt \\
&= \frac{\epsilon^{(\log 2)^\delta}}{\underline{\epsilon}(\omega)} \left\{ \frac{\epsilon^4}{2} \left[ t O\left(t (\log^{1/t})^\Delta\right) \right]_0^{\pi/\omega} + \left[ O\left((\log^{1/t})^\Delta\right) \right]_{\pi/\omega}^{\pi} \right\} \\
&+ O(\omega) \left[ O\left(t (\log^{1/t})^\Delta\right) \right]_0^{\pi/\omega} + O(1) \left[ O\left((\log^{1/t})^\Delta\right) \right]_{\pi/\omega}^{\pi} \\
&= O(1) + O\left((\log \omega)^\Delta\right) = O\left((\log \omega)^\Delta\right)
\end{aligned}$$

Therefore

$$\pi \frac{d}{d\omega} \bar{\sigma}_1(\omega) = \frac{\pi D}{(\omega)} \left\{ \frac{\epsilon(\omega) \log \omega}{\delta (\log \log \omega)^{\delta-1}} + O\left( \frac{\epsilon(\omega) \log \omega}{(\log \log \omega)^{2(\delta-1)}} \right) \right\} \\ + \epsilon \cdot O((\log \omega)^\Delta)$$

On account of the fact that  $\frac{(\log \log \omega)^{\delta-1}}{(\log \omega)^{1-\Delta}} \rightarrow 0$ , as  $\omega \rightarrow \infty$ ,

we have

$$\pi \frac{d}{d\omega} \bar{\sigma}_1(\omega) = \frac{D}{\omega} + D \cdot O\left( \frac{1}{\omega (\log \log \omega)^{\delta-1}} \right) + o\left( \frac{1}{\omega} \right)$$

$$\int_{\omega}^{2\omega} \frac{d}{dx} \bar{\sigma}_1(x) dx = \frac{D}{\pi} \int_{\omega}^{2\omega} \frac{1}{x} dx + D \cdot o\left( \int_{\omega}^{2\omega} \frac{1}{x (\log \log x)^{\delta-1}} dx \right) \\ + o\left( \int_{\omega}^{2\omega} \frac{1}{x} dx \right) \\ = \frac{D}{\pi} \log 2 + o(1),$$

by Lemma 2 (ii).

Hence, the theorem is proved.

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ON THE DERIVATIVE OF MEIJER'S G-FUNCTION AND  
MACROBERT'S E-FUNCTION

By

V. M. BHISE

*Department of Mathematics, G. S. Technological Institute, Indore (M. P.)*

[Received on 23rd January, 1962]

1. Varma (6, p. 209) has introduced a generalisation of the Laplace transform

$$(1.1) \quad \phi(s) = s \int_0^\infty e^{-st} f(t) dt$$

in the form

$$(1.2) \quad \phi(s) = s \int_0^\infty (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) f(t) dt.$$

On putting  $k + m = \frac{1}{2}$  relation (1.2) reduces to (1.1). We denote (1.2) symbolically by

$$\phi(s; k, m) = W[f(t); k, m].$$

In this paper we have obtained some formulae for the  $n^{th}$  differentiation of Meijer's G-function and MacRobert's E-function. In one case we have used a known theorem involving (1.2).

2. Rathic (5, p. 391) has shown that if

$$\phi(s; k, m; \lambda) = W[x^\lambda h(x); k, m],$$

then

$$(2.1) \quad \frac{d^n}{ds^n} \left\{ -\frac{1}{s} \phi(s; k, m; \lambda) \right\} = \frac{(-1)^n}{s} \phi(s; k + \frac{1}{2}n, m - \frac{1}{2}n; \lambda + n)$$

provided the integrals involved are uniformly convergent and  $n$  is a positive integer.  
Take

$$x^\lambda h(x) = x^\lambda \cdot G_{p-2, q-1}^{l, u-2} \left( \beta x \left| \begin{matrix} a_3, \dots, a_p \\ b_1, \dots, b_{q-1} \end{matrix} \right. \right),$$

then (3, p. 275),

$$\phi(s; k, m; \lambda) = s^{-\lambda} \cdot G_{p, q}^{l, u} \left( \frac{\beta s}{s} \left| \begin{matrix} -\lambda, -\lambda - 2m, a_3, \dots, a_p \\ b_1, \dots, b_{q-1}, -\lambda + k - m - \frac{1}{2} \end{matrix} \right. \right),$$

$$p+q < 2(l+u-1); R(b_j + \lambda + 1 + m \pm m) > 0, j = 1, 2, \dots, l;$$

$$|\arg \frac{s}{\beta}| < (l+u-\frac{1}{2}p-\frac{1}{2}q-1)\pi.$$

Using this in (2.1), replacing  $-\lambda$  by  $a_1$ ,  $-\lambda - 2m$  by  $a_2$  and  $-\lambda + k - m - 1/2$  by  $b_q$ , we get

$$(2.2) \quad \frac{dn}{ds^n} \left[ s^{a_1-1} G_{p,q}^{l,u} \left( \frac{\beta}{s} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] = (-1)^n \cdot s^{a_1-n-1} \cdot$$

$$\times G_{p,q}^{l,u} \left( \frac{\beta}{s} \left| \begin{matrix} a_1-n, a_2, \dots, a_p \\ b_1, \dots, \dots, b_q \end{matrix} \right. \right)$$

As  $G$ -function is symmetrical in  $a_1, \dots, a_u$ , formula (2.2) is equivalent to  $u$  different relations.

3. We verify here the formula (2.2) from the definition of  $G$ -function and state three more formulae of the same type.

(i) Using the definition of  $G$ -function (1, p. 207) we have,

$$\begin{aligned} & \frac{dn}{dx^n} \left[ x^{a_1-1} \cdot G_{p,q}^{l,u} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] \\ &= \frac{1}{2\pi i} \int_L \frac{\prod_{j=1}^l \frac{\pi}{q} \Gamma(b_j - s)}{\prod_{j=l+1}^u \frac{\pi}{p} \Gamma(1 - b_j + s)} \frac{\prod_{j=1}^u \frac{\pi}{p} \Gamma(1 - a_j + s)}{\prod_{j=u+1}^p \frac{\pi}{q} \Gamma(a_j - s)} \beta^s \cdot \Gamma(1 - a_1 + s) \frac{dn}{ds} (x^{a_1-1-s}) ds \\ &= (-1)^n \cdot x^{a_1-n-1} \cdot G_{p,q}^{l,u} \left( \frac{\beta}{x} \left| \begin{matrix} a_1-n, a_2, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \end{aligned}$$

(ii) We now use the definition of  $G$ -function (1, p. 208) involving the hypergeometric function. This yields on differentiating inside the sign of summation,

$$\begin{aligned} & \frac{dn}{dx^n} \left[ x^{a_1-1} G_{p,q}^{l,u} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] \\ &= \sum_{h=2}^u \frac{\frac{u}{p} \frac{\pi}{q} \Gamma(a_h - a_1)}{\frac{u}{p} \frac{\pi}{q} \Gamma(a_h - a_h + 1)} \frac{\prod_{j=1}^l \frac{\pi}{q} \Gamma(b_j - a_h + 1)}{\prod_{j=l+1}^p \frac{\pi}{q} \Gamma(a_h - b_j)} \beta^{a_h-1}. \end{aligned}$$

$$\begin{aligned}
& \sum_{r=0}^{\infty} \frac{\frac{q}{\pi} (1 + b_j - a_h)_r (-1)^r (q-l-u)}{\prod_{j=1}^p (1 + a_j - a_h)_r \beta^r L_r} \cdot \frac{dx^n}{dx^n} \cdot x^{a_1 - a_h + r} \\
& + \frac{\frac{u}{\pi} \Gamma(a_1 - a_j) \prod_{j=1}^l \Gamma(b_j - a_1 + 1) \beta^{a_1 - 1}}{\prod_{j=u+1}^p \Gamma(a_j - a_1 + 1) \prod_{j=l+1}^q \Gamma(a_1 - b_j)} \\
& \sum_{r=0}^{\infty} \frac{\frac{q}{\pi} (1 + b_j - a_1)_r (-1)^r (q-l-u)}{\prod_{j=2}^p (1 + a_j - a_1)_r \beta^r L_r} \cdot \frac{dx^n}{dx^n} \cdot x^r.
\end{aligned}$$

Now, in the first term we apply a property (4, p. 32) of factorial function in the form,

$$\frac{1}{(1 - a_1 - a_h)} \cdot \frac{(-1)^n \Gamma(a_h - a_1 + n)}{\Gamma(a_h - a_1) (a_1 - n - a_h + 1)_r}$$

and in the second term replace  $r - n$  by  $r$ . On some simplification we get the desired result.

The three other formulae-like (2.2), which can be obtained in a similar way, are

$$(3.1) \quad \frac{dx^n}{dx^n} \left[ x^{a_p - 1} G_{p, q}^{l, u} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] = x^{a_p - n - 1} G_{p, q}^{l, u} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_{p-1}, a_p - n \\ b_1, \dots, b_q \end{matrix} \right. \right)$$

$$(3.2) \quad \frac{dx^n}{dx^n} \left[ x^{-b_1} G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] = (-1)^n x^{-b_1 - n} G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a_p \\ b_1 + n, b_2, \dots, b_q \end{matrix} \right. \right)$$

and

$$(3.3) \quad \frac{dx^n}{dx^n} \left[ x^{-b_q} G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] = x^{-b_q - n} G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a \\ b_1, \dots, b_{q-1}, b_q + n \end{matrix} \right. \right)$$

4. Here we obtain some results for MacRobert's *E*-function with the help of (2.2), (3.1), (3.2) and (3.3).

(i) From (2.2) we have,

$$\begin{aligned}
& \frac{dx^n}{dx^n} \left[ x^{a_1 - 1} G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_{q+1} \\ b_1, \dots, b_q \end{matrix} \right. \right) \right] = (-1)^n x^{a_1 - n - 1} \\
& \quad \times G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} a_1 - n, a_2, \dots, a_{q+1} \\ b_1, \dots, b_q \end{matrix} \right. \right)
\end{aligned}$$

Using a property of  $G$ -function (1, p. 209), we obtain,

$$\frac{d^n}{dx^n} \cdot G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} 1, a_2 - a_1 + 1, \dots, a_{q+1} - a_1 + 1 \\ b_1 - a_1 + 1, \dots, b_p - a_1 + 1 \end{matrix} \right. \right) = \frac{(-1)^n}{\beta^n} \cdot$$

$$\times G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} 1, a_2 - a_1 + 1 + n, \dots, a_{q+1} - a_1 + 1 + n \\ b_1 - a_1 + 1 + n, \dots, b_q - a_1 + 1 + n \end{matrix} \right. \right)$$

Replacing  $a_{j+1} - a_1 + 1$  by  $\beta_j$ ,  $j = 1, 2, \dots, q$ ;  $b_i - a_1 + 1$  by  $\alpha_i$ ,  $i = 1, 2, \dots, p$  and applying the relation (1, p. 215) we get

$$(4.1) \quad \frac{d^n}{dx^n} \cdot E \left\{ \begin{matrix} \alpha_1, \dots, \alpha_p \\ \beta_1, \dots, \beta_q \end{matrix} ; \frac{\beta}{x} \right\} = \frac{(-1)^n}{\beta^n} \cdot E \left\{ \begin{matrix} a_1 + n, \dots, a_p + n \\ \beta_1 + n, \dots, \beta_q + n \end{matrix} ; \frac{\beta}{x} \right\}$$

With  $\frac{\beta}{x} = y$  and  $n = 1$ , we have a known result (2, p. 260).

(ii) From (2.2) we have, with necessary changes,

$$\begin{aligned} \frac{d^n}{dx^n} \left[ x^{a_1 - 1} G_{q+1, p}^{p, 1} \left( \frac{x}{\beta} \left| \begin{matrix} 1 - b_1, \dots, 1 - b_{q+1} \\ 1 - a_1, \dots, 1 - a_p \end{matrix} \right. \right) \right] &= (-1) \cdot x^{a_1 - n - 1} \cdot \\ &\times G_{q+1, p}^{p, 1} \left( \frac{x}{\beta} \left| \begin{matrix} 1 - b_1, \dots, 1 - b_{q+1} \\ 1 - a_1 + n, 1 - a_2, \dots, 1 - a_p \end{matrix} \right. \right) \end{aligned}$$

Applying again the properties (1, p. 209), (1, p. 215), replacing  $1 - b_{j+1} + b_1$  by  $\beta_j$ ,  $j = 1, 2, \dots, q$  and  $1 - a_i + b_1$  by  $\alpha_i$ ,  $i = 1, 2, \dots, p$  we obtain a known result (5, p. 393)

$$(4.2) \quad \frac{d^n}{dx^n} \left[ x^{-a_1} E \left\{ \begin{matrix} \alpha_1, \dots, \alpha_p \\ \beta_1, \dots, \beta_q \end{matrix} ; \frac{x}{\beta} \right\} \right] = (-1)^n x^{-a_1 - n} E \left\{ \begin{matrix} \alpha_1 + n, \alpha_2, \dots, \alpha_p \\ \beta_1, \dots, \beta_q \end{matrix} ; \frac{x}{\beta} \right\}$$

(iii) Taking (3.1) in the form,

$$\begin{aligned} \frac{d^n}{dx^n} \left[ x^{a_{q+1} - 1} G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_{q+1} \\ b_1, \dots, b_p \end{matrix} \right. \right) \right] &= x^{a_{q+1} - n - 1} \\ &\times G_{q+1, p}^{p, 1} \left( \frac{\beta}{x} \left| \begin{matrix} a_1, \dots, a_q, a_{q+1} - n \\ b_1, \dots, b_p \end{matrix} \right. \right) \end{aligned}$$

simplifying as in the above case, setting  $b_i - a_1 + 1 = \alpha_i, i = 1, 2, \dots, p$  and  $a_{j+1} - a_1 + 1 = \beta_j, j = 1, 2, \dots, q$  we have

$$(4.3) \quad \frac{d^n}{dx^n} \left[ x^{\beta_q - 1} \cdot E \left\{ \begin{array}{c} a_1, \dots, a_p \\ \beta_1, \dots, \beta_q \end{array} ; \frac{\beta}{x} \right\} \right] = x^{\beta_q - n - 1} E \left\{ \begin{array}{c} a_1, \dots, \dots, \dots, a_p \\ \beta_1, \dots, \beta_{q-1}, \beta_q - n : \frac{\beta}{x} \end{array} \right\}$$

Proceeding on similar lines as above, the formulae (3.2) and (3.3) yield again the formulae (4.1), (4.2) and (4.3).

5. We now state some elementary relations for G-function involving different combinations of its parameters. We have chosen the combinations by considering the symmetry of the parameters involved in the function.

In (2.2), put  $n = 1$  and  $s = \frac{1}{x}$  to yield,

$$(5.1) \quad x \frac{d}{dx} G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) = G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1 - 1, a_2, \dots, a_p \\ b_1, \dots, \dots, \dots, b_q \end{array} \right. \right) \\ + (a_1 - 1) G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right)$$

which is a known result (1, p. 210).

Similarly with  $n = 1$  and  $s = \frac{1}{x}$  we have, from (3.1),

$$(5.2) \quad x \frac{d}{dx} G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) = (a_p - 1) G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \\ - G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, a_2, \dots, a_{p-1}, a_p - 1 \\ b_1, \dots, \dots, \dots, b_q \end{array} \right. \right)$$

Also with  $n = 1$ , (3.2) and (3.3) yield, respectively, the relations

$$(5.3) \quad x \frac{d}{dx} \cdot G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) = b_1 \cdot G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \\ - G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, \dots, a_p \\ b_1 + 1, b_2, \dots, b_q \end{array} \right. \right)$$

and

$$(5.4) \quad x \frac{d}{dx} G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) = b_q G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \\ + G_{p, q}^{l, u} \left( \beta_x \left| \begin{array}{c} a_1, \dots, \dots, \dots, a_p \\ b_1, \dots, b_{q-1}, b_q + 1 \end{array} \right. \right)$$

Subtracting (5.1) from (5.2) we get,

$$(5.5) \quad (a_p - a_1) \quad G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) = G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1 - 1, a_2, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \\ + G_{p, q}^{l, u} \left( \beta x \left| \begin{matrix} a_1, \dots, a_p - 1 \\ b_1, \dots, b_q \end{matrix} \right. \right)$$

This is a known relation (1, p. 210).

Again subtracting (5.1) from (5.3) we have, a known result (1, p. 209). We can have four other relations, like (5.5), obtained by subtracting (5.2) from (5.3) and (5.4) from (5.1), (5.2), (5.3) respectively.

I wish to express my thanks to Dr. B. R. Bhonsale for his help and guidance in the preparation of this paper, and to Principal V. H. Acharya for the facilities he gave to me.

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RELATIONS BETWEEN HANKEL TRANSFORM AND THE  
GENERALISED LAPLACE TRANSFORMS

(Whittaker & Meijer Transforms)

By

S. P. SINGH

*Department of Mathematics, Banaras Hindu University, Varanasi-5*

[Received on February 8, 1962]

1. The Laplace transform of a function  $f(t) \in L(0, \infty)$  is defined by the equation

$$L[f, p] = \int_0^\infty e^{-pt} f(t) dt; \quad R(p) > 0; \quad (1.1)$$

while its Hankel transform of order by the equation

$$H_\nu [f; \xi] = \int_0^\infty t f(t) J_\nu (\xi t) dt; \quad \xi > 0. \quad (1.2)$$

Tricomi [8] discovered a relation between the Hankel and Laplace transforms. Recently Bhonsle [1] has obtained a relation between the Laplace transform of  $t^\mu f(t)$  and the Hankel transform of  $f(t)$ . Verma [10] has obtained relations between the Hankel transform and the generalised Laplace transform. The object of this note is to establish relations between the Hankel transform and the generalised Laplace transforms (Whittaker and Meijer-transforms).

Whittaker transform is defined by [9]

$$W_{k, m} [f; p] = \int_0^\infty (2px)^{-\frac{1}{2}} W_{k, m}(2px) f(x) dx; \quad R(p) > 0. \quad (1.3)$$

The Meijer transform has been given in the form [5]

$$W_{k + \frac{1}{2}, m} [f; p] = \int_0^\infty e^{-\frac{1}{2}pt} W_{k + \frac{1}{2}, m}(pt) (pt)^{-k - \frac{1}{2}} f(t) dt, \quad R(p) > 0 \quad (1.4)$$

When  $k = \frac{1}{2}$ ,  $m = \pm 1/4$ , (1.3) reduces to (1.1) and (1.4) reduces to (1.1), when  $k = m$ .

2. *Theorem 1* :—If  $f(t)$  and  $H_\nu [f; \xi]$  belongs to  $L(0, \infty)$  and if  $R(p) > 0$ ,  $|p| > |\xi|$  and  $(\mu + \nu \pm m + 5/4) > 0$ ;

$$\text{then } W_{k, m} [t^\mu f; p] = \int_0^\infty \chi(p, \xi) H_\nu [f; \xi] d\xi; \quad (2.1)$$

$$\text{Where } \chi(p, \xi) = \sum_{r=0}^{\infty} \frac{\left(\frac{\xi}{2}\right)^{\nu+2r+1}}{r! \Gamma(1+\nu+r)} \frac{\Gamma \times \left(\mu + \nu + 2r \pm m + \frac{5}{4}\right)}{\Gamma(\mu + \nu + 2r - k + 7/4)} (2p)^{-\mu - \nu - 2r} \\ \times {}_2F_1 \left( \begin{matrix} \mu + \nu + 2r \pm m + 5/4 \\ \mu + \nu + 2r - k + 7/4 \end{matrix}; \frac{1}{2} \right). \quad (2.2)$$

*Proof:*—Since  $f(t)$  belongs to  $L(0, \infty)$ , we have by Hankel's Inversion theorem [7]

$$f(t) = \int_0^\infty \xi H_\nu [f; \xi] J_\nu(t\xi) d\xi \quad (2.3)$$

Multiplying both the sides by  $t^\mu (2pt)^{-1/4} W_{k, m}(2pt)$  and integrating between  $(0, \infty)$ , we have after inverting the order of integration, which is permissible due to the absolute convergence of the integrals involved under the conditions stated in the theorem,

$$W_{k, m}[t^\mu f; p] = \int_0^\infty \xi H_\nu [f; \xi] W_{k, m}[t^\mu J_\nu(\xi t); p] d\xi.$$

Now,

$$W_{k, m}[t^\mu J_\nu(\xi t); p] = \sum_{r=0}^{\infty} \frac{(\xi/2)^{\nu+2r}}{r! \Gamma(1+\nu+r)} \frac{\Gamma \times (\mu + \nu + 2r \pm m + 5/4)}{\Gamma(\mu + \nu + 2r - k + 7/4)} \xi^\mu \\ \times 2^{-(\mu + \nu + 2r + 1)} \times p^{-(\mu + \nu + 2r)} {}_2F_1 \left( \begin{matrix} \mu + \nu + 2r \pm m + 5/4 \\ \mu + \nu + 2r - k + 7/4 \end{matrix}; \frac{1}{2} \right),$$

which we obtain with the help of an integral given by Bose [2] in this way

$$W_{k, m}[x^n; p] = \frac{\Gamma \times (n \pm m + 5/4)}{\Gamma(n - k + 7/4) 2^{n+1}} {}_2F_1 \left[ \begin{matrix} n \pm m + 5/4 \\ n - k + 7/4 \end{matrix}; \frac{1}{2} \right]$$

provided that  $\pm m + 5/4 > 0$ ,  $R(p) > 0$ .

Hence the result follows.

**Particular case 1:** When  $k = 1/4$ ,  $m = \pm 1/4$ , we get a well-known result due to Bhonsle, viz.

$$L[t^\mu f; p] = \int_0^\infty k(p; \xi) H_\nu [f; \xi] d\xi,$$

$$\text{where } k(p; \xi) = \Gamma(\mu + \nu + 1) \xi (p^2 + \xi^2)^{-\frac{1}{2}} (\mu + 1) \frac{p - \nu}{\mu} \left( \frac{p}{\sqrt{p^2 + \xi^2}} \right).$$

$$R(\mu) > -1, R(\mu + \nu) > -1, R(p) > 0.$$

Example:— Let  $f(t) = t^{m-1} e^{-at}$

$$\text{Then } H_\nu [f; \xi] = \Gamma(m+\nu+1) (a^2 + \xi^2)^{-\frac{1}{2}} (m+1) \frac{p^{-\nu}}{m} \left( \frac{a}{\sqrt{a^2 + \xi^2}} \right).$$

$$W_{k, m} [t^\mu f; p] \text{ [(by Bose, 2)]}.$$

$$= \sum_{r=0}^{\infty} \frac{(-a)^r}{r!} \frac{\Gamma \times (\mu+m+r \pm m+1/4)}{\Gamma(\mu+m+r-k+3/4)} \frac{p^{(1-\mu-m-r)}}{2^{\mu+m+r}} \times \\ \times {}_2F_1 \left( \begin{matrix} \mu+m+r \pm m 1/4 \\ \mu+m+r-k+3/4 \end{matrix}; \frac{1}{2} \right).$$

Therefore, by the theorem, we have,

$$\int_0^\infty \xi^{\mu+1} \Gamma(m+\nu+1) (a^2 + \xi^2)^{-\frac{1}{2}} (m+1) \frac{p^{-\nu}}{m} \left( \frac{a}{\sqrt{a^2 + \xi^2}} \right) \times \\ \times \sum_{r=0}^{\infty} \frac{(\xi/2)^{\nu+2r}}{r!} \frac{\Gamma \times (\mu+\nu+2r \pm m 5/4)}{\Gamma(\mu+\nu+2r-k+7/4)} (2p)^{-(\mu+\nu+2r)} \\ \times {}_2F_1 \left( \begin{matrix} \mu+\nu+2r \pm m+5/4 \\ \mu+\nu+2r-k+7/4 \end{matrix}; \frac{1}{2} \right) d\xi \\ = \sum_{r=0}^{\infty} \frac{(-a)^r}{r!} \frac{\Gamma \times (\mu+m+r \pm m+1/4)}{\Gamma(\mu+m+r-1-k+7/4)} \frac{p^{(1-\mu-\nu-r)}}{2^{\mu+\nu+r}} \cdot \\ \cdot {}_2F_1 \left[ \begin{matrix} \mu+m+r \pm m+1/4 \\ \mu+m+r-1-k+7/4 \end{matrix}; \frac{1}{2} \right]$$

where  $\mu+\nu \pm m+5/4 > 0$ ,  $\mu+m \pm m+1/4 > 0$ .

3. Theorem 2. If  $f(t)$  and  $H_\nu [f; \xi]$  belongs to  $L(0, \infty)$  and if  $R(\mu+\nu-k+1 \pm m) > 0$  and  $R(p), R(\xi) > 0$ , then

$$W_{k+\frac{1}{2}, m} [t^\mu f; p] = \int_0^\infty \chi(p, \xi) H_\nu [f; \xi] d\xi, \quad (3.1)$$

Where

$$\chi(p, \xi) = \frac{\xi^{\nu+1} \Gamma \times (\mu+\nu-k+1 \pm m)}{2^\nu \Gamma(\mu+\nu-2k+1) \Gamma(\nu+1)} p^{-\mu-\nu-1} \times$$

$${}_4F_3 \left\{ \begin{array}{c} \frac{\mu+\nu-k+1\pm m}{2}, \frac{\mu+\nu-k+2\pm m}{2} \\ \nu+1, \frac{\mu+\nu+1-2k}{2}, \frac{\mu+\nu-2k+2}{2} \end{array} ; \frac{-\xi^2}{p^2} \right\}.$$

The proof is similar to theorem (1) given above. The result follows, since Jaiswal [4] has given that

$$W_{k+\frac{1}{2}, m} [t^{\mu} J_{\nu} (\xi t) ; p] = \frac{\xi^{\nu} \Gamma(\mu+\nu-k+1\pm m)}{2^{\nu} \Gamma(\mu+\nu-2k+1) \Gamma(\nu+1)} p^{-\mu-\nu-1} \times$$

$${}_4F_3 \left\{ \begin{array}{c} \frac{\mu+\nu-k+1\pm m}{2}, \frac{\mu+\nu-k+2\pm m}{2} \\ \nu+1, \frac{\mu+\nu-2k+1}{2}, \frac{\mu+\nu-2k+2}{2} \end{array} ; \frac{-\xi^2}{p^2} \right\} \quad (3.2)$$

where  $R(\mu+\nu-k+1\pm m) > 0$ ,  $R(p) > 0$ ,  $|p| > |\xi|$ .

Again, on putting  $k=m$ ,  ${}_4F_3$  degenerates into  ${}_2F_1$  giving Bhonsle's result as before.

*Example* :—If  $f(t) = t^{1-2\mu} G_{p, q}^{l, m} \left( \lambda t^2 \left| \begin{array}{c} \alpha_1, \alpha_2, \dots, \alpha_p \\ \beta_1, \beta_2, \dots, \beta_q \end{array} \right. \right)$ .

$$\text{We get } H_{\nu} [f; \xi] = \frac{2-2\mu}{\xi^{3-2\mu}} G_{p+2, q}^{l, m+1} \left( \frac{4\lambda}{\xi^2} \left| \begin{array}{c} \mu-1/2-\nu/2, \mu-1/2+\nu/2, \alpha_1, \dots, \alpha_p \\ \beta_1, \beta_2, \dots, \beta_q \end{array} \right. \right).$$

Where  $p+q < 2(l+m)$ ,  $R(\alpha_j - \mu) < -1/4$ ;  $j=1, 2, 3, \dots, m$ .

$|\arg \lambda| < (l+m-p/2-q/2)\pi$ ,  $R(\beta_j - \mu + \nu/2) > -3/2$ ,  $j=1, 2, \dots, l$ .

By Mehra [6], we have

$$W_{k+\frac{1}{2}, m} [t^{\mu} f ; p] = \frac{p^{\mu-2}}{\sqrt{\pi} 2^{\mu-1-2k-2m}} \times$$

$$G_{p+4, q+2}^{l, m+4} \left( \frac{4\lambda}{p^2} \left| \begin{array}{c} \frac{k+\mu-1\pm m}{2}, \frac{k+\mu\pm m}{2}, \alpha_1, \dots, \alpha_p \\ \beta_1, \dots, \beta_q, \frac{\mu-1}{2}+k, \frac{\mu}{2}+k \end{array} \right. \right).$$

$$|\arg \frac{p}{\lambda}| < (l+m - \frac{p}{2} - \frac{q}{2})\pi, p+q+1 < 2(l+m).$$

$$R(\frac{\mu}{2} - \frac{1}{2} + k \pm m) < R(\beta_j), j=1, 2, \dots, l.$$

Hence, we get.

$$\begin{aligned}
 & \int_0^\infty \frac{\xi^p + 1}{2^p} \frac{\Gamma(\mu + \nu - k + 1 \pm m)}{\Gamma(\mu + \nu - 2k + 1) \Gamma(\nu + 1)} P^{-\mu - \nu - 1} \\
 & {}_4F_3 \left[ \begin{matrix} \frac{\mu + \nu - k + 1 \pm m}{2}, \frac{\mu + \nu - k + 2 \pm m}{2} \\ \nu + 1, \frac{\mu + \nu + 1 - 2k}{2}, \frac{\mu + \nu - 2k + 2}{2} \end{matrix} ; \frac{-\xi^2}{p^2} \right] \\
 & \times \frac{2^{2-2\mu}}{\xi^{3-2\mu}} G_{p+2, q}^{\mu, m+1} \left( \frac{4\lambda}{\xi^2} \middle| \begin{matrix} \mu - 1/2 \pm \nu/2, \alpha_1, \alpha_2, \dots, \alpha_p \\ \beta_1, \beta_2, \dots, \beta_q \end{matrix} \right) d\xi. \\
 & = \frac{p^{\mu-2}}{\sqrt{\pi} 2^{\mu-1-2k-2m}} G_{p+4, q+2}^{\mu, m+4} \\
 & \left( \frac{4\lambda}{p^2} \middle| \begin{matrix} \frac{k+\mu-1 \pm m}{2}, \frac{k+\mu \pm m}{2}, \alpha_1, \dots, \alpha_p \\ \beta_1, \beta_2, \dots, \beta_q, \frac{\mu-1}{2} \pm k, \frac{\mu}{2} + k \end{matrix} \right).
 \end{aligned}$$

The author wishes to express his grateful thanks to Dr. Brij Mohan, for his guidance and valuable help in the preparation of this note.

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## A NOTE ON THE ADSORPTION OF THIOCYANATE IONS BY SOILS AND COMPOST

By

S. G. MISRA and A. L. MISRA

*Chemistry Department, University of Allahabad, Allahabad*

[Received on 9th July, 1961]

### ABSTRACT

Appreciable amounts of  $\text{CNS}^-$  ions are adsorbed by soils and compost from very dilute solutions of potassium and ammonium thiocyanates. However, compost shows the maximum adsorption. Normal soil and the acid soil show adsorption in the decreasing order.

The organic matter content, pH and calcium carbonate appear to influence the adsorption of  $\text{CNS}^-$  ions. The leaching of the  $\text{CNS}^-$  ions, consequently the hazard of  $\text{CNS}^-$  toxicity increase if large amount of organic matter is present or if acidic soils are limed moderately.

Sodium and ammonium thiocyanates have been used as weedicides and defoliants for a long time. These thiocyanates when sprayed get access into the soil and after years of application, tend to accumulate there in appreciable amounts. So far, no work appears to have been done on the nature of adsorption of thiocyanate ions when they come in contact with the soil or organic material though the residual toxic effects of applied thiocyanates are on record (1).

The present studies were made with a view to find out the fate of thiocyanate ions when they are mixed with soils or a material rich in organic matter either singly or in the presence of free calcium carbonate and potassium nitrate.

### EXPERIMENTAL PROCEDURE

Two soils were selected for adsorption experiments—an acid soil and a normal soil,—with a view to find out the effect of pH of soils on the adsorption of thiocyanate ions. The acid soil was obtained from Agricultural Research Institute, Kanke, Ranchi, Bihar. It had a pH of 5.2, it belonged to red soil group, was deficient in calcium and phosphorus whilst the normal soil was collected from the Muir Central College Compound, University of Allahabad. It had a pH of 7.4, was well supplied with calcium and phosphorus. The soils were powdered, passed through a 70 mesh sieve and analysed for their chemical constituents using standard methods (2). (vide table 1)

TABLE 1  
Chemical analysis of soils (%)

Chemical constituents.	Acid soil	Normal soil
Loss on ignition	3.49	3.88
HCl - insoluble	84.51	81.64
Sesquioxides	11.45	11.17
$\text{Fe}_2\text{O}_3$	4.18	4.12
CaO	0.10	0.99
MgO	Trace	1.16
$\text{P}_2\text{O}_5$	Trace	0.08
$\text{K}_2\text{O}$	0.41	0.73
Total carbon	0.325	0.40
Total carbonates	Nil	1.24
Exchangeable - $\text{H}^+$	1.1 m.e.	-
Exchangeable - $\text{Ca}^{++}$	-	12.23

TABLE 2 (A)  
Adsorption of  $\text{CNS}^-$  from KCNS by soils and compost  
5gms. soils or compost + 50ml. solution

Concentration of KCNS $(\times 10^{-2}\text{N})$	Adsorption of $\text{CNS}^-$ by 5 gms. of the materials in mgms		
	Acid soil	Normal soil	Compost
0.9950	1.97	3.30	5.68
0.4975	1.21	1.91	3.89
0.3316	0.98	1.51	3.00
0.2487	0.90	1.39	2.67
0.1990	0.79	1.21	2.38

TABLE 2 (B)

Effect of  $\text{CaCO}_3$  and  $\text{KNO}_3$  on the adsorption of  $\text{CNS}^-$  from KCNS by soils and compost.

5gms. soils or compost + 0.1 gm salts + 50ml. solution

Concentration of KCNS $(\times 10^{-2} \text{N})$	Adsorption of $\text{CNS}^-$ in the presence of salts (mgms)					
	Calcium carbonate			Potassium nitrate.		
	Acid soil	Normal soil	Compost	Acid soil	Normal soil	Compost
0.9950	2.5	4.5	6.20	3.30	4.64	5.91
0.4975	2.55	2.84	3.25	2.00	2.55	3.86
0.3316	1.85	2.08	2.32	1.50	2.00	2.72
0.2487	1.48	1.68	1.85	1.19	1.50	2.26
0.1990	1.45	1.39	1.56	1.00	1.27	1.85

TABLE 3 (A)

Adsorption of  $\text{CNS}^-$  from  $\text{NH}_4\text{CNS}$  by soils and compost

5gms. soils or compost + 50ml. solution

Concentration of $\text{NH}_4\text{CNS} (\times 10^{-2} \text{N})$	Adsorption of $\text{CNS}^-$ by 5gms of the materials (mgms).		
	Acid soil	Normal soil	Compost
0.9950	2.14	3.53	5.85
0.4975	1.33	2.32	3.65
0.3316	1.10	2.00	2.84
0.2487	0.93	1.68	2.26
0.1990	0.87	1.33	1.85

TABLE 3 (B)

Effect of  $\text{CaCO}_3$  and  $\text{KNO}_3$  on the adsorption of  $\text{CNS}^-$  from  $\text{NH}_4\text{CNS}$  by soils and compost

5gms. soils of compost + 0.1 gm salts + 50ml. solution

Concentration of $\text{NH}_4\text{CNS}$ ( $\times 10^{-2}$ N)	Adsorption of $\text{CNS}^-$ in the presence of salts (mgms)					
	Calcium carbonate			Potassium nitrate		
	Acid soil	Normal soil	Compost	Acid soil	Normal soil	Compost
0.9950	2.86	4.58	6.43	3.43	4.69	6.20
0.4975	1.74	2.90	3.53	2.26	2.55	3.42
0.3316	1.45	2.08	2.55	1.62	2.03	2.49
0.2487	1.39	1.62	2.03	1.45	1.68	2.03
0.1990	1.16	1.45	1.68	1.27	1.16	1.62

The compost was well humified sample and was collected from a local pit. It had a slightly acidic reaction and contained 5.35% total carbon.

The thiocyanates used were potassium and ammonium thiocyanates of A. R. quality. A stock solution of these two of approximately 0.01N concentration was prepared and standardised for CNS content. Then further dilutions upto 0.002N were made and used for adsorption experiments.

5 gms. of the soils or compost were weighed in 250 ml. conical flasks, 50 ml. of the thiocyanate solutions were added, the contents were shaken for  $\frac{1}{2}$  hour and kept overnight. They were filtered through a Buchner funnel fitted with a filter paper, connected to a filter pump. The residue left on the filter paper was washed with 25 ml. distilled water to wash any adhering thiocyanate and the amount of thiocyanate was found out in the whole of the filtrate. The amount of thiocyanate in the blank experiments, run simultaneously was also determined. The difference denoted the amount of adsorbed  $\text{CNS}^-$  by soils or compost.

In order to find out the effect of free calcium carbonate and potassium nitrate on the adsorption of thiocyanates by soils or compost, 0.1 gm. of the salts were added in solid form to 5 gm. soils or compost and the adsorption experiments were repeated as before.

The thiocyanate was determined volumetrically following the method of Volhards (3), because the direct titration of thiocyanate with  $\text{AgNO}_3$  using ferric alum as indicator is not satisfactory. During titration the precipitated silver thiocyanate occludes ferric thiocyanate and the end point is difficult to recognise. Hence, excess of silver nitrate was added to the filtrates containing thiocyanates. and then the indicator was introduced. The unused silver nitrate was back-titrated with standard thiocyanate solution. The results obtained by this method were quite satisfactory.

## DISCUSSION

The foregoing results clearly show that greatest amount of  $\text{CNS}^-$  ions are held up by the compost, whilst the least amount by the acid soil. The normal soil shows an intermediate behaviour. It is also evident that more of  $\text{CNS}^-$  are held by soils from  $\text{NH}_4\text{CNS}$  than from KCNS of same strength.

The addition of calcium carbonate and potassium nitrate has a marked effect on the adsorption of  $\text{CNS}^-$  by soils, whilst very little effect is observed on the absorption by compost. Potassium nitrate appears to affect an enhanced absorption of  $\text{CNS}^-$  ions in the case of soils when  $\text{NH}_4\text{CNS}$  is used than when KCNS for adsorption.

From our observations the following informations are obtained :

(1) That the percentage of  $\text{CNS}^-$  removed from thiocyanates of ammonium and potassium is appreciable. At the highest and lowest concentration of potassium thiocyanate used the acid and the normal soils adsorb not less than 7.14 and 11.5—21% of the added  $\text{CNS}^-$  respectively, the compost adsorbing 20.41%. Still greater adsorption is observed when KCNS is replaced by  $\text{NH}_4\text{CNS}$ .

(2) The addition of calcium carbonate helps in a futher increase in the adsorption of  $\text{CNS}^-$  from thiocyanates of potassium and ammonium. Potassium nitrate affects the adsorption less efficiently especially in soils.

(3) A high organic matter content, specially in compost, leads to larger amount of  $\text{CNS}^-$  adsorption. In this way the composts differ strikingly from the soils (which contain only a small percentage of organic matter).

The acid soil shows a lesser adsorption than the normal soil, perhaps due to its lower pH value. The addition of calcium carbonate greatly improves its pH and consequently the adsorption increases. The normal soil and the compost, which are practically neutral, record a less distinct increase in adsorption as a result of calcium carbonate addition. Potassium nitrate affects the adsorption but to a lesser degree.

From these observations it may be concluded that the application of thiocyanate year after year accumulates  $\text{CNS}^-$  in soils, which is toxic to plants and microorganisms. This accumulation is greatly assisted by the addition of organic matter and by liming the acid soil or by the addition of salts like  $\text{KNO}_3$ . In other words, the leaching of  $\text{CNS}^-$  is greatly reduced by the addition of organic matter, liming material or a salt like  $\text{KNO}_3$  to soils. Thus an acidic soil which has least tendency to accumulate the injurious  $\text{CNS}^-$  ions may accumulate more of them after liming. The organic soils and compost have the probability of affecting the plants and microbes to the highest extent as they adsorb and consequently store the maximum amount of  $\text{CNS}^-$  ions. The liming and addition of  $\text{KNO}_3$  to organic soils and compost heaps will have a very little affect in increasing this amount.

The adsorption of inorganic thiocyanates by soils can be minimised by restricting their use to acidic soils alone. Their use in organic or calcareous soils may lead to greater adsorption of  $\text{CNS}^-$  ions.

The adsorption of  $\text{CNS}^-$  by soils may be due to the presence of calcium carbonate which helps in precipitating out calcium thiocyanate which is less soluble than  $\text{NH}_4$  or K-thiocyanate.

Further experiments are in progress to cause a reduced adsorption of inorganic thiocyanate by soils and compost.

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# PHOTOCHEMICAL NITRIFICATION IN BENTONITE MEDIUM

By

S. P. TANDON, S. K. DE and R. C. RASTOGI

*Chemical Laboratories, University of Allahabad, Allahabad*

[Received on 17th March, 1962]

## ABSTRACT

Photochemical nitrification in bentonite medium (without any additional carbonate) with different ammonium salts exposed to sunlight and to 1000 Watt electric light has been studied. No nitrification was observed in the dark. In light, the nature of non-biological nitrification in bentonite medium was observed to depend on the time of exposure, the nature of light source and the anionic part of the ammonium salt.

In two previous communications (1,2) we have reported that *Nitrosomonas* can be cultured in bentonite medium, provided it is supplied with optimum amounts of magnesium or calcium carbonates and a source of energy preferably ammonium sulphate. The nitrifying bacteria can also be developed in bentonite medium in the presence of only ammonium salts even if there is no calcium or magnesium carbonate supplied (3), although in both the cases the extent of their growth is not as high as when one of the carbonates and ammonium sulphate are added in our proposed medium. It has also been observed in our previous work (3) that on bentonite surface the anionic part of an ammonium salt determines considerably the measure of the biological transformation of the ammonium radical to nitrite.

In this paper, we have made an attempt to see whether it is possible to obtain photochemical nitrification of the ammonium radical on bentonite surface and if so, to see whether the anions associated with an ammonium salt have any effect on the nitrification process.

## EXPERIMENTAL

The bentonite sample (Kashmir) was obtained from the collection of the late Dr. S. P. Mitra who identified it by means of X-ray diffraction. The clay mineral was first finely powdered in an agate mortar and then passed through a 100 mesh-sieve. The pulverised mineral so obtained was then stocked in bottles for the experiments.

For the study of photochemical nitrification on bentonite surface, each mixture containing 1.0 g. bentonite, an ammonium salt (amount corresponding to 0.0212 g. nitrogen) was taken in a 250 ml. Jena flask and was sterilized in an autoclave for half an hour at 15 lbs pressure. After sterilization, the flasks were left for cooling.

One set out of three sets of the conical flasks was covered with a black cloth and kept within a wooden box of suitable size. To avoid any possible source of light, the wooden box was also covered with another similar piece of cloth.

The flasks of other sets were exposed to sunlight daily for eight hours (9 A. M. to 5 P. M.). Any loss of moisture from the flasks due to evaporation was made up by adding daily the necessary quantity of sterilized distilled water.

The flasks of the third sets were kept daily for eight hours under 1000 Watt electric bulb. The loss of moisture from the flasks due to heat of the electric bulb was similarly made up.

Before each estimation, the flasks were placed in an incubator maintained at 35°C.

The amount of nitrite formed photochemically was estimated colorimetrically after the completion of every 48 hours by a Duboscq colorimeter using 0.5%  $\alpha$ -naphthylamine and 0.8% sulphanilic acid solution in acetic acid (sp. gr. 1.04).

Chromate and phosphate ions have been observed to interfere with the determination of nitrite and these were removed before each estimation by treating the solution with barium chloride and ferric chloride respectively.

#### RESULTS AND DISCUSSIONS

In the dark we have not observed any nitrification on bentonite surface. The results presented in table 1, however, show that photochemical nitrification does occur in bentonite medium, provided the mixtures are exposed to sunlight for a longer duration of time. This is also true for the mixtures kept under a 1000 Watt electric bulb. The extent of conversion of ammonium radical to nitrite seems to be influenced by the nature of the anion associated with it.

TABLE 1

*Effect of sunlight on the process of nitrification in bentonite medium in presence of ammonium salts*

Ammonium salts.	Nitrite concentration mg/litre				
	144	192	240	288	336
1. $(\text{NH}_4)_2\text{CO}_3$	—	—	—	0.575	0.639
2. $(\text{NH}_4)_2\text{H}_2\text{PO}_4$	—	—	—	—	Traces
3. $(\text{NH}_4)_2\text{SO}_4$	—	—	—	—	Traces
4. $(\text{NH}_4)_2\text{HPO}_4$	—	—	—	—	Traces
5. $\text{CH}_3\text{COONH}_4$	—	—	—	—	Traces
6. $\text{NH}_4\text{C}_6\text{H}_5\text{O}_7$	—	—	—	Traces	0.639
7. $\text{NH}_4\text{OH}$	—	—	—	—	—
8. $\text{NH}_4\text{NO}_3$	—	—	—	—	Traces
9. $(\text{NO}_3)_3\text{AsO}_4$	—	—	—	—	—

We have seen that the carbonate anion offers least resistance to the transformation of the ammonium nitrogen to nitrite nitrogen in bentonite medium. No nitrification was observed with the halides, oxalate, thiosulphate, chromate, molybdate, arsenate, thiocyanate and monohydrogen phosphate of ammonium.

TABLE - 2

*Effect of artificial light (1000 Watt) on the process of nitrification in bentonite medium in presence of ammonium salts.*

Ammonium Salts	Nitrite concentration mg/litre				
	Time in hours				
	144	192	240	288	336
1. $(\text{NH}_4)\text{H}_2\text{PO}_4$	—	—	—	0.6590	0.833
2. $(\text{NH}_4)_2\text{SO}_4$	—	—	—	0.865	1.000
3. $(\text{NH}_4)_2\text{HPO}_4$	—	—	—	Trace	0.7371
4. $(\text{NH}_4)_2\text{CrO}_7$	—	—	—	—	0.639
5. $\text{CH}_3\text{COONH}_4$	—	—	—	—	Traces
6. $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$	—	—	—	—	Traces
7. $\text{NH}_4\text{NO}_3$	0.575	0.575	0.675	0.7917	1.288
8. $(\text{NH}_4)_3\text{AsO}_4$	—	—	—	Traces	Traces
9. $\text{NH}_4\text{OH}$	—	—	—	—	Traces

From the table 2 it may be seen that under the electric bulb there is a tendency of the ammonium radicals to be nitrified much more readily than under the impact of sun heat. This is due to the variations in the availability of energy from the two sources which result in the activation of the molecules differently and hence the difference in the extent of the process. It is well known that chemical or physical changes result either in the production of energy in the system which radiates out into the surroundings or in the absorption of energy from the surroundings. All reactions are, therefore, considerably influenced by the nature and the extent of energy available around them.

From the results recorded in this paper it will be seen that the oxidation of ammonium salts to nitrite by light takes place on the whole to a very small extent. This might be due to greater thermochemical stability of ammonium salts as compared to nitrites.

#### ACKNOWLEDGMENT

We express our thanks to the Scientific Research Committee, U. P., for providing a research scholarship to one of the authors (R. C. Rastogi) and thus enabling him to carry out this research work.

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# STUDIES ON THE COAGULATION OF SILVER IODIDE SOL, PART I

By

S. S. UPPAL and S. GHOSH

Chemical Laboratories, Allahabad University, Allahabad

[Received on 15th June, 1962]

## ABSTRACT

Smoluchowski in 1916, considered coagulation to be a result of the aggregation, resulting from the collisions of the discharged dispersed units. His equation relating the number of aggregated particles left with the time  $t$ , has been found to fail in the region of slow coagulation. Several other relationships connecting the time of coagulation with the concentration of the electrolyte have been described and Reerink and Overbeek obtained a relation by considering the potential energy of interaction between two charged particles.

This paper deals with the applicability of a general equation for the aggregation process similar to that for a chemical reaction. This has been verified for a silver iodide sol coagulated by different concentrations of electrolytes. The values for the energy of activation and also the relative values of the steric factor have been obtained. It has further been shown that all other relationships connecting the time of coagulation with the concentration of the electrolyte, are similar to the one proposed here.

## INTRODUCTION

The stability of a lyophobic sol is attributed chiefly to the electric charge on the colloidal units. The addition of an electrolyte lowers the surface potential, and the collisions of these particles result in their aggregation, which finally separate out as a precipitate when they have attained a certain size. The amount of an electrolyte affecting the coagulation of a lyophobic sol is related to the time of coagulation and there is usually a minimum concentration of an electrolyte below which no coagulation occurs within a reasonable time.

Various equations (1) have been suggested correlating the concentration of an electrolyte with the time required for coagulation of a lyophobic sol of a definite concentration. Fuchs (4) considered the potential energy of interaction between the two charged particles and Reerink and Overbeek (9) proposed the relationship

$$\log W = - k_1 \log C + k_2 \quad \dots (1)$$

In the above equation,  $W$  is the ratio between the rate of rapid coagulation to that of slow coagulation and is often noted as stability factor. Since the rate of rapid coagulation, where no energy of interaction takes place, is usually constant, we may conclude

$$\log t = - \alpha \log C + \beta \quad \dots (2)$$

where  $t$  is the time of coagulation by the addition of concentration  $C$ , of an electrolyte and  $\alpha$  and  $\beta$  are constants.

It should be recalled that Smoluchowski (11) considered coagulation to be a rate process but his equation, relating the number of aggregated particles left with time  $t$ , fails in the region of slow coagulation.

This paper deals with the consideration that coagulation is a rate process and that the rate may be denoted by the equation

$$-\frac{dn}{dt} = P_z e^{-E/RT} \quad \dots(3)$$

where  $P$  is the steric factor,  $z$  is the number of collisions per unit time between the particles present in a unit volume and  $E$  is the energy of activation of the particles leading to successful collisions for aggregation.

In the following pages the effect of temperature on the lyophobic sol of silver iodide on its time of coagulation, in the presence of different concentrations of electrolytes are given, and the energy of activation has been calculated.

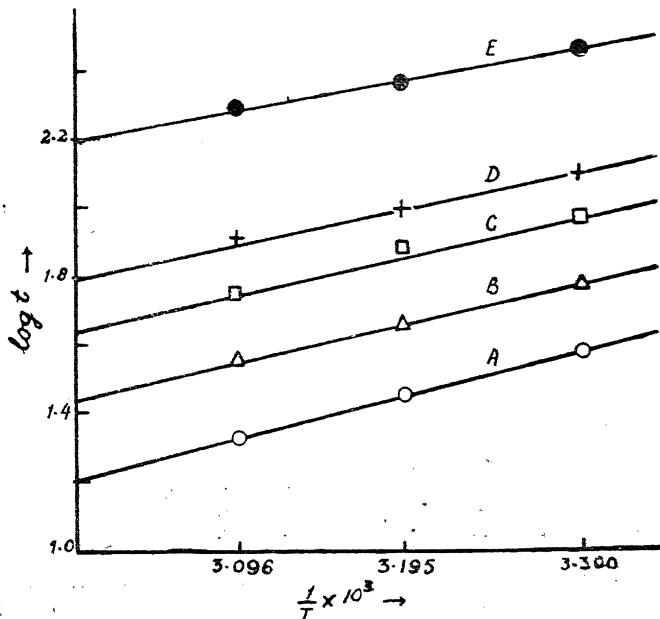


Fig. 1. Plot of  $\log t$  against  $1/T \times 10^3$

A : 0.160 gM/l  $\text{KNO}_3$ ; B : 0.152 gM/l  $\text{KNO}_3$ ; C : 0.144 gM/l  $\text{KNO}_3$ ;  
D : 0.136 gM/l  $\text{KNO}_3$ ; E : 0.120 gM/l  $\text{KNO}_3$ .

#### EXPERIMENTAL

Silver iodide sol was prepared by adding 200 ml of 0.1 N silver nitrate (B. D. H.) to 250 ml of 0.1 N potassium iodide (E. Merck extra pure). The latter was shaken after each addition of silver nitrate and finally the total volume was raised to 1250 ml with distilled water. The sol thus prepared was left undisturbed for 48 hours and it was found that the coagulation values of electrolytes showed very slight variation due to ageing of the sol after this time.

2.0 ml of the sol was taken in each one of a series of clean and dry test tubes. In another series of test tubes were taken different amounts of the precipitating electrolyte, in which distilled water was added in order to keep the total

volume 8.0 ml. These tubes were then kept in a thermostat at 30°C, till they attained the temperature of the bath. The sol and the electrolyte were then mixed and the time of aggregation of the colloidal particles to such a size as could not pass through the pores of Whatman filter paper No. 44 was determined. The results were within 6% error for the observations made for the same sol. Similar experiments were repeated at 40°C and 50°C. Columns 2, 3 and 4 of tables I, II and III show the values of  $\log t$  at 30°C, 40°C and 50°C where  $t$  is the time of coagulation in minutes. In figures 1, 2 and 3 are plotted the values of  $\log t$

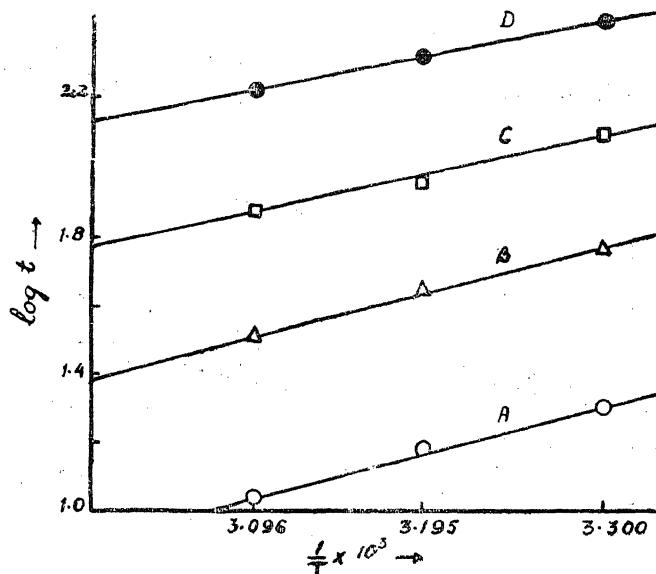


Fig. 2. Plot of  $\log t$  against  $1/T \times 10^3$   
 A : 2.50 mgM/l Ba (NO<sub>3</sub>)<sub>2</sub>; B : 2.30 mgM/l Ba (NO<sub>3</sub>)<sub>2</sub>  
 C : 2.10 mgM/l Ba (NO<sub>3</sub>)<sub>2</sub>; D : 1.90 mgM/l Ba (NO<sub>3</sub>)<sub>2</sub>

against  $1/T$  for the electrolytes potassium nitrate (A. R.) barium nitrate (A. R.) and aluminium nitrate (Riedel, G. P.) respectively. Different sets of straight lines are obtained with different coagulating electrolytes. Each straight line refers to one concentration of the coagulating electrolyte used for studying the time of coagulation at 30°C, 40°C and 50°C.

#### *Calculation of the energy of activation E and the relative values of the steric factor P.*

The aggregation of the colloidal particles proceeds upto a certain size for the observed time  $t$ . This leads to a decrease in the number of the particles present in the unit volume of the sol. Hence the average rate by which the number of the particles per unit volume decrease by the process of aggregation may be taken as proportional to  $1/t$ . Therefore,

$$-\frac{dn}{dt} = \frac{k}{t} = Pz e^{-E/RT},$$

$$\frac{1}{t} = \frac{1}{k} Pz e^{-E/RT},$$

or

$$\text{or } \log t = - \log K P z + \frac{E}{2.303 R T} \quad \dots (4)$$

where  $K = 1/k = \text{constant}$ .

The average value of the energy of activation for the process of coagulation is determined from the slope of the straight line obtained by plotting  $\log t$  against  $1/T$ . The average value of  $K P z$  is then determined by substituting the corresponding values of  $E$ ,  $T$  and  $t$  in equation (4). As the value of  $z$  should be the

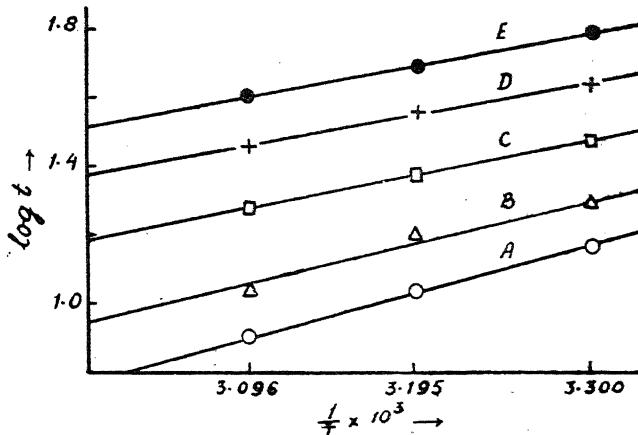


Fig. 3. Plot of  $\log t$  against  $1/T \times 10^3$

A : 0.0277 mgM/l  $\text{Al}(\text{NO}_3)_3$ ; B : 0.0267 mgM/l  $\text{Al}(\text{NO}_3)_3$ ; C : 0.0257 mgM/l  $\text{Al}(\text{NO}_3)_3$ ; D : 0.0246 mgM/l  $\text{Al}(\text{NO}_3)_3$ ; E : 0.0236 mgM/l  $\text{Al}(\text{NO}_3)_3$ .

same for the same sol coagulated by different concentrations of the coagulating electrolyte the variations in the value of  $K P z$  are due to the changes in the value of the steric factor  $P$  only. The values of  $E$  and  $K P z$  are recorded in columns 5 and 6 respectively of tables I, II and III.

*Effect of temperature on the coagulation of silver iodide sol with coagulating electrolytes potassium nitrate, barium nitrate and aluminium nitrate.*

TABLE I  
Coagulating electrolyte — Potassium nitrate

Potassium nitrate gM/l	Values of $\log t$			$E$ Cals.	$K P z$
	30°C	40°C	50°C		
0.160	1.5682	1.4472	1.3222	5492	245.5
0.152	1.7709	1.6532	1.5563	5034	71.6
0.144	1.9590	1.8808	1.7404	4919	38.7
0.136	2.0969	1.9912	1.9031	4576	15.6
0.120	2.4564	2.3617	2.2788	3890	2.2

TABLE II  
Coagulating electrolyte -- Barium nitrate

Barium nitrate mgM/l	Values of $\log t$			E Cals.	KPz
	30°C	40°C	50°C		
2.50	1.3010	1.1761	1.0414	5950	963.8
2.30	1.7634	1.6435	1.5051	5722	231.7
2.10	2.0934	1.9542	1.8751	4805	23.7
1.90	2.4065	2.3096	2.2201	4119	3.7

TABLE III  
Coagulating electrolyte -- Aluminium nitrate

Aluminium nitrate mgM/l	Values of $\log t$			E Cals	KPz
	30°C	40°C	50°C		
0.0277	1.1761	1.0414	0.9031	6179	1879
0.0267	1.3010	1.2041	1.0414	5492	451.9
0.0257	1.4771	1.3802	1.2788	4691	78.3
0.0246	1.6532	1.5682	1.4624	4348	30.3
0.0236	1.7993	1.6990	1.6128	4348	21.4

#### RESULTS AND DISCUSSION

Hurd and Latteron (8) investigated the effect of temperature on the time of set of silicic acid gels. Similar studies have been made for the gelation of several inorganic gels by Ghosh and coworkers (5). The energy of activation for the process of gelation has been calculated by these workers in the same way, as it is done for chemical reactions. The specific rate constant for a chemical reaction is given by the relation

$$k_r = A e^{-E/RT}$$

... (5)

where  $A$  is the frequency factor, and has been identified to be equal to  $Z$  or collision number. It is well known that in several cases the observed reaction rates are far less than those calculated by this equation and hence Hinshelwood (7) suggested the equation

$$k_r = Pz e^{-E/RT} \quad \dots (6)$$

where  $P$  is called the steric factor and is the measure of the deviation of the actual reaction from the ideal behaviour of the simple collision theory. According to the concept of absolute reaction rates the value of  $P$  is related with the entropy of activation for the activated complex formed as an intermediary step for a chemical change. For smaller values of  $P$ , the entropy of activation is usually negative. In the chemical reactions of the oppositely charged ions the value of  $\Delta S$  (entropy of activation) has been found to be large, while this is small for the reaction between similarly charged ions. When a sol is treated with a smaller amount of an electrolyte and the coagulation is slow, the charge on the colloidal units may not be completely removed, so much so that the aggregation process involves the collisions of the similarly charged units. The charge on the colloidal surface is due to the adsorption of ions and for the partially discharged colloidal units the collisions occurring at the spots which are least covered by electric charge will lead to aggregation. In other words, for such a case the collisions resulting into aggregation must be directed along such specific spots and the value of  $P$  or steric factor will be small. In this connection it should be noted that Eyring and Stern (3) showed that the kinetics of the denaturation of proteins investigated by Evans and Jenkins (2) is attended with an increase in entropy for the activated complex. Obviously for the aggregation process this will tend to decrease. Thus if we assume that the value of  $P$  of equation (4) is a function of the concentration of the added electrolyte, we have

$$\log t = \frac{E}{2.303 RT} - \log Kz - a \log C \quad \dots (7)$$

putting  $P = C^a$

It will be noted that if  $z$  remains constant for a given amount of sol to be aggregated to the same stage of coagulation, the above is

$$\log t = \frac{E}{2.303 RT} - a \log C - k' \quad \dots (8)$$

so that this equation is similar to the various relations obtained previously connecting the time of coagulation with the concentration of the coagulation electrolyte provided the value of  $E$  or the energy of activation remains constant with all the concentrations of electrolyte added for coagulation.

The data recorded here show that the values of  $E$  slightly increase with the increasing concentration of the electrolyte (within the limits of concentrations used in the experiments). But there is a considerable increase in the value of  $P$  with the increasing amounts of the electrolytes used for coagulation and therefore, it is clear that the value of  $P$  is related with the residual electric charge left on the colloidal particles.

It should, however, be noted here that with the continued aggrégation, at each stage the particles of different sizes and aggregation are taking part in coagulation. At each stage the colliding species are different and hence the values of both  $P$  and  $E$  may differ. As early as 1918, Westgren (12) noted that in the aggregation process of gold sol the rate becomes unusually slow when the coarser particles appear in the system. Very recently Ghosh and Singh (10) showed that hydrous ferric oxide sols containing coarser particles have higher energy of activation than the sols having finer ones. Thus the heat of activation leading to growth of particles increases with the increasing aggregated state of colloidal units, so that the value of  $E$  necessarily changes considerably throughout the process of aggregation till the coagulation is complete. In the coagulation process the speed of aggregation becomes slow as it approaches the state of flocculation. Hence when larger amounts of an electrolyte are used the rate of aggregation becomes fast because of the considerable decrease in the electric charge on the colloidal particles so that the later stage of aggregation is comparatively slow and therefore, it becomes prominent in defining the rate of coagulation. It is for this reason that the energy of activation increases slightly with the increasing concentration of the coagulating electrolyte.

It is worthwhile to mention here that an equation very similar to (2) is obtainable from Smoluchowski's relation :

$$\Sigma n = \frac{n_0}{1 + \varepsilon K n_0 t} \quad (9)$$

where  $\varepsilon$  is less than unity for partially discharged particles. Assuming that for a given sol containing  $n_0$  particles coagulation occurs when this number after attaining a certain stage of aggregation has decreased to  $\Sigma n$  after time  $t$ , we have

$$1 + \varepsilon K n_0 t = \text{constant}$$

$$\text{or} \quad \varepsilon t = \text{constant}$$

$\varepsilon$  depends for a given amount of a sol upon the charge density of the colloidal units and therefore the concentration of the added electrolyte so that we have

$$\frac{k_1}{C} t = k_2 \quad \text{putting } \varepsilon = \frac{k_1}{C}$$

where  $k_1$  and  $k_2$  are constants.

$$\text{or } \log t = - k_1 \log C + k'_2$$

It should, however, be made clear that it has been assumed that there is a decrease in the charge of the colloidal units immediately after the addition of the electrolyte. This may be true when larger concentrations of the electrolyte are used but for smaller concentrations the charge neutralization may also have a speed (6) in which case the value of  $P$  is likely to change. In such a circumstance the simple relation connecting the time of coagulation with the concentration of the electrolyte may fail. This explains why the relation (2) may not be strictly applicable to both slow and rapid ranges and straight line relationship of  $\log C - \log t$  cannot be observed for all the concentrations of the electrolyte used for coagulation.

## CONCLUSION

It may be concluded that the aggregation process in coagulation is similar to chemical reactions, aggregation occurring due to the collisions of the colloidal units. The chief difference is that with the progressive aggregation the aggregated units are not completely out of picture.

The value of  $P$  or  $\Delta S$  (entropy of activation) is related to the residual electric charge on the colloidal units. The energy of activation increases with the increasing size of the aggregates.

Further work in this direction will follow in a subsequent publication.

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## GALLATE COMPLEX OF MANGANESE (II)

By

M. S. KACHHAWAHA and ARUN K. BHATTACHARYA

Department of Chemistry, University of Saugor, Saugor (M. P.)

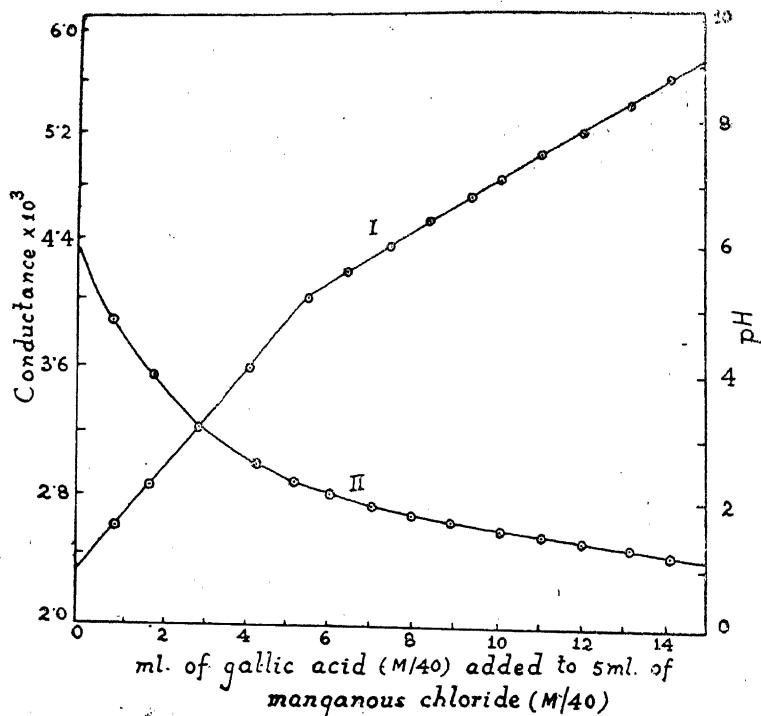
[Received on 10th October, 1962]

### ABSTRACT

The system manganese chloride - gallic acid in aqueous solution has been studied by pH, conductance and absorption measurements utilizing the method of monovariation and the Job's method of continuous variation. The investigations reveal the presence of only one 1:1 complex whose value of dissociation constant has been calculated to be  $6.95 \times 10^{-3}$  at  $25^{\circ}\text{C}$ . Different colour reactions have been seen at different concentrations. A probable structure has also been assigned to the complex.

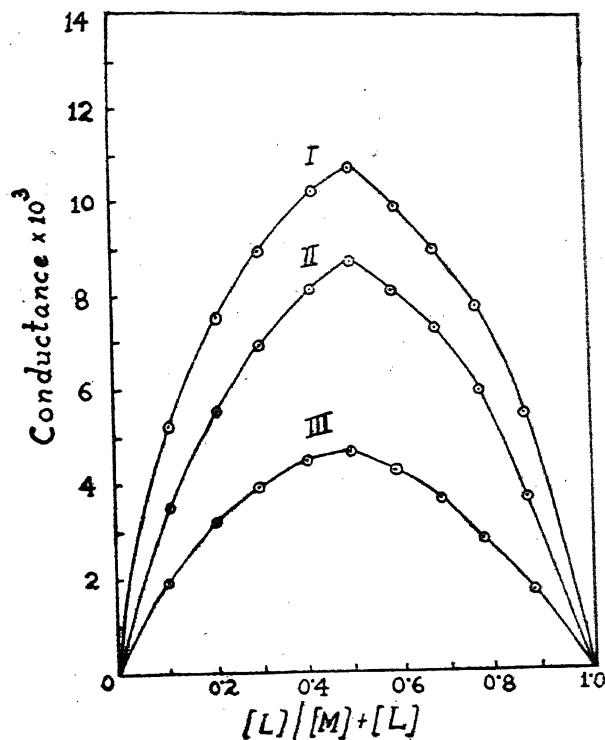
Gallic acid is reported to give colour reaction with titanium,<sup>1</sup> uranium,<sup>2</sup> cerium<sup>3</sup> and the rare earths.<sup>4</sup> It also gives colour or precipitate with copper,<sup>5</sup> bismuth<sup>6</sup> and lead,<sup>7</sup> forming complexes in all the cases. Fernandes<sup>8</sup> has mentioned three distinct complexes of molybdic oxide with potassium gallate in the ratio 0.66, 1 and 2 moles of gallate per mole of  $\text{MoO}_3$ . But no effort has so far been made to investigate into the nature of reaction that the above ligand undergoes

Fig. 1



with manganous salts. The authors, therefore, during the physico-chemical study of Mn complexes of hydroxy acids,<sup>9-11</sup> thoroughly studied the reaction of gallic acid with manganese chloride taking recourse to such physico-chemical methods as pH, conductance and spectrophotometry utilising the monovariation method<sup>12</sup> and the continuous variation method.<sup>13</sup>

Fig. 2



#### EXPERIMENTAL

pH measurements were made with a Beckman pH meter, model G. Doran's conductivity bridge was used for conductance measurements and spectrophotometric measurements were done using a Beckman model DU spectrophotometer using 0.5ml. quartz absorption cells. Gallic acid E. Merck, G. R. was recrystallised and dried at 120°C. Manganous chloride B. D. H. Analar was employed and fresh solutions were prepared with double distilled water. Throughout the course of investigations the temperature was maintained at  $25 \pm 0.1^\circ\text{C}$  by means of an electrically operated thermostat.

#### Composition of the complex :

The composition of the complex was ascertained by the monovariation method<sup>12</sup>. To a constant volume of manganous chloride solution increasing amounts of the solution of gallic acid were added and the changes in conductance and pH were plotted against the corresponding amount of gallic acid added (Fig. 1

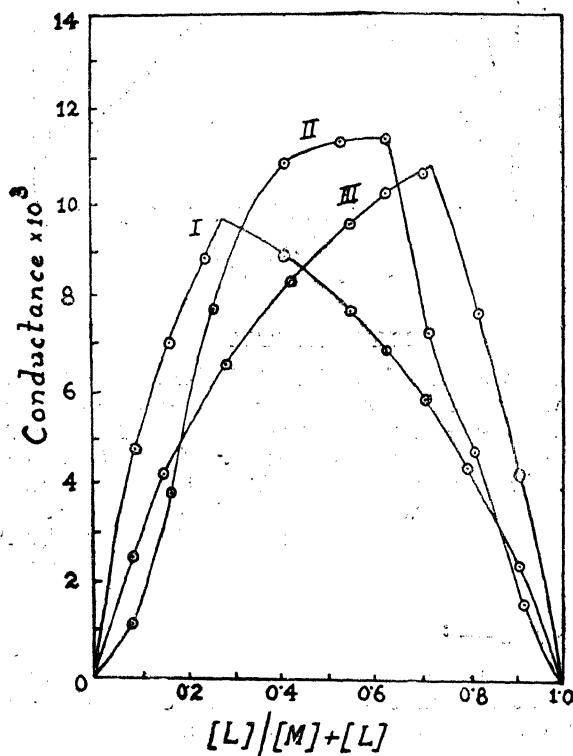
curves I & II). Both the pH and the conductance curves indicate only one inflection corresponding to the composition of the complex in which the molar ratio of the ligand and manganese chloride is 1:1, showing thereby that only a 1:1 complex is formed.

The above composition of the manganese gallate complex was verified by the Job's method of continuous variation,<sup>13</sup> utilising conductance and spectrophotometry as the index properties. The way of using the method has been described elsewhere<sup>14</sup>. According to the continuous variation method in the formation of a chelate compound  $A_m B_n$  where A is metallic ion and B is a chelating agent,  $m A + nB = A_m B_n$  ;

$$= \frac{(A_m B_n)}{(A)^m (B)^n}$$

If the restriction,  $(A) + (B) = C$ , where C is a constant, is imposed, then it can be very easily shown that for a constant total concentration of metal and chelating agents, the concentration of chelate is greatest when the metal and the chelating agents are brought together in the same ratios in which they exist in the solution. Therefore a series of solutions were prepared in which the molar ratios of manganese to gallic acid were varied but the total molarity of the two was always maintained constant and the difference in the index property of the mixture over the sum of that of the metal ion and the ligand for no reaction between the two,

Fig. 3

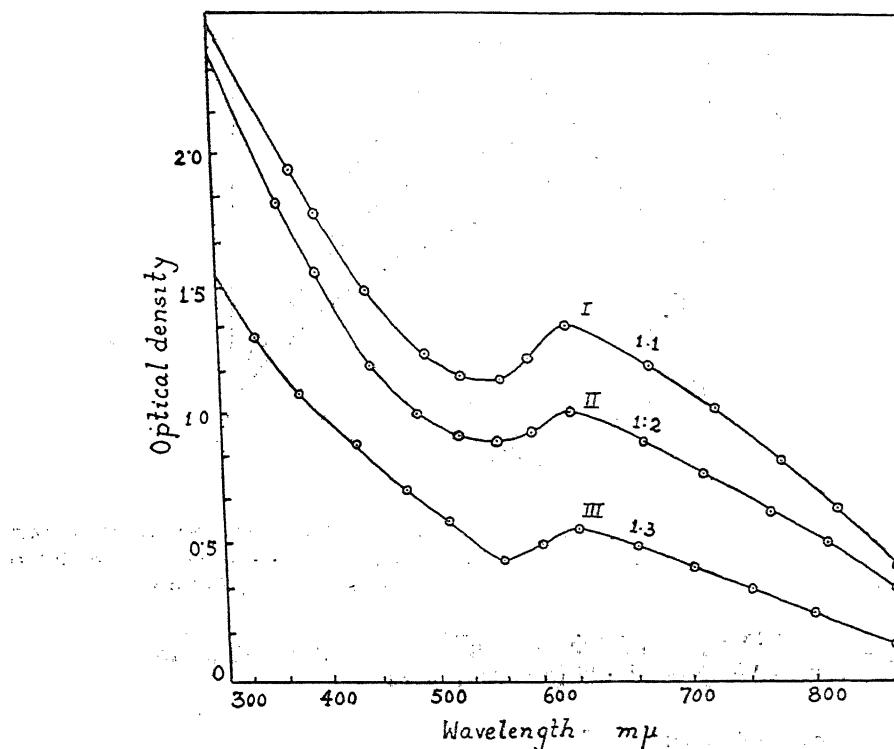


was plotted against the corresponding composition of the mixture. The maxima in the curves (Figs. 2 & 5) confirmed the stoichiometry obtained by the monovariation method.

An interesting observation during the course of our study was that whereas no colour developed when the two reagents were mixed at higher concentrations an intense green colour developed at very high dilution ( $5 \times 10^{-4}$  M) after the mixtures were kept for twelve hours.

Since the coloured complex shows selective absorption at the wavelength (600  $m\mu$ ) irrespective of the composition of the mixture as shown in Fig. 4, it is confirmed that the formation of more than one complex is out of question. The continuous variation method was, therefore, tried at the above mentioned characteristic wavelength as well as at other wavelengths. (Fig. 4).

Fig. 4

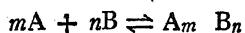


In the continuous variation method where spectrophotometry was taken as an index property, the optical density values of the various mixtures were plotted against the corresponding compositions as the complex was the only coloured species.

All the foregoing experimental observations lead us to the definite conclusion that manganese (II) forms only a 1 : 1 complex with gallic acid.

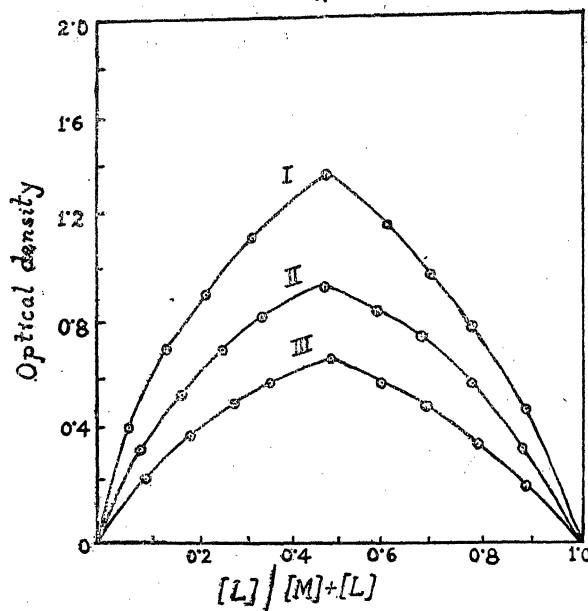
### Dissociation constant of the complex :

Job's method of continuous variation for the study of imperfect complexes using an additive molar property as guide is very reliable in the reactions of the type



where A is a metallic ion and B is a chelating agent.

Fig. 5



The method is, however, applicable only in such cases where only one complex is formed. For such sorts of reactions Job has derived an equation for determining the instability constant of the complex. The equation is

$$K = \frac{c^{m+n-1} \cdot p^{n-1} [(pm + n)x - n]^{m+n}}{m^{n-1} \cdot n^{m-1} \cdot (p - 1)^{m+n-1} [n - (m + n)x]}, \text{ which reduces to}$$

$$K = \frac{c [(p + 1)x - 1]^2}{(p - 1)(1 - 2x)}$$

in the case of a 1 : 1 complex

Where  $c$  = Concentration of the metal ion

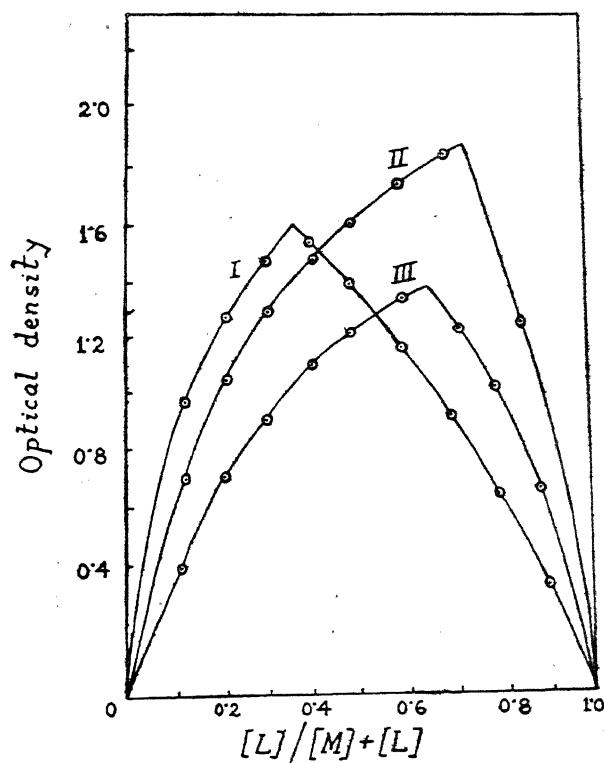
$p$  = ratio of the concentration of the metal ion and the ligand,

$x$  = molar fraction of the ligand used

and  $K$  = dissociation constant of the complex.

Hence the dissociation constant of the complex was determined utilising the above equation and employing nonequimolar solutions.  $x$  was determined from the maxima of the curves. Electrical conductance and optical density data (Figs. 3 & 6) help to arrive at the value of dissociation constant. In Fig. 3 the curves I-III have been obtained for three different molar concentrations of the reagents used whereas the curves I-III of the Fig. 6 represent the data obtained, for three different wavelengths but the same molar concentrations. The dissociation constant has been found to be  $6.95 \times 10^{-3}$  at  $25^{\circ}\text{C}$ .

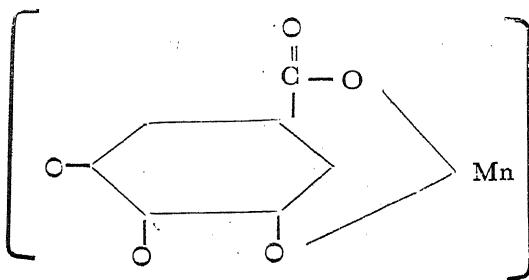
Fig. 6



#### Structure of the complex :

It is quite probable that the colour development at higher dilutions is due to hydrolysis which causes a drop in pH and hence facilitates the liberation of protons

from the acid, helping thus the chelation of the metal ion with the ligand. Hence the following structure has been assisted to the complex.



The authers express their thanks to Professor A. K. Bhattacharya, for the interest he took in the present work.

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## STUDIES ON THE COAGULATION OF SILVER IODIDE SOL, PART II

By

S. S. UPPAL and S. GHOSH

Chemical Laboratories, Allahabad University, Allahabad

[Received on 15th June, 1962]

### ABSTRACT

In this paper the effect of dilution of negatively charged silver iodide sol on the coagulation values of electrolytes in the presence of different amounts of the peptising agent potassium iodide, has been studied. The coagulation values for infinite and one hour of observation were determined graphically and the results are given here. It has also been shown that adsorption of the iodide ions follow Freundlich adsorption rule in imparting the electric charge on the colloidal particles of silver iodide. These investigations were carried out potentiometrically using  $\text{Ag}(\text{s})$ ,  $\text{AgI}(\text{s})$ , I electrode. From the results it may be concluded that desorption of the stabilising ions from the colloidal surface occurs on dilution making the sol unstable.

### INTRODUCTION

Change in concentration of a sol causes a variation of the coagulating power of an electrolyte and Burton and Bishop (1) concluded that it decreases for the monovalent ions, remains almost constant for the bivalent ions while for the trivalent ions it increases as the sol is diluted. This rule is not true for every sol and Ghosh and Dhar (4) while investigating the above phenomenon observed that the sols of hydrous oxides of tin, iron, aluminium and chromium showed a decrease of coagulation values on dilution with all the coagulating ions.

Kruyt and van der Spek (5) pointed out that the dilution of a sol results in the decrease of concentration which would normally require lesser electrolyte per unit volume to produce charge neutralization and coagulation, but at the same time the number of collisions per unit time between the particles would decrease. It is, therefore, necessary to add more electrolyte to the dilute sol in order to compensate the probability of adhesion. The predominance of one factor over the other defines the effect of dilution of the sol.

According to Weiser and Nicholas (9) and Ghosh and Dhar (3), the coagulating power of an electrolyte depends upon the preferential adsorption of the ions of both like and opposite sign. The Burton Bishop rule according to these workers is the result of the specific properties of the electrolyte added and the dispersed particles.

Coagulating power of an electrolyte determined experimentally varies enormously for a sol with the time allowed for the interaction of the electrolyte and the colloidal particles. We have, in this paper, studied the effect of dilution on the coagulation values of the nitrates of potassium, barium and aluminium for the negative silver iodide sols peptised with different amounts of potassium iodide for the various times of interaction. The coagulation values have also been extrapolated for infinite time of observation. Incidentally, it has been shown that iodide ions are adsorbed by silver iodide particles and follow Freundlich adsorption rule (2) showing that the stability of the sol may also be affected by variation in the adsorption of the peptising ions by silver iodide when the sol is diluted.

## EXPERIMENTAL

Five samples of silver iodide sol A, B, C, D and E each containing 0.016 gram mole per litre of silver iodide and 0.0012, 0.0020, 0.0040, 0.0060 and 0.0080 gram mole respectively of an excess of potassium iodide were prepared by the interaction of potassium iodide (E. Merck extra pure) and silver nitrate (B. D. H.) solutions. Potassium nitrate thus produced in the system was present and its amount is the same as that of silver iodide present in the sols. These sols were then diluted to half and one third concentrations and the coagulation values were determined at 30°C by mixing 2 ml of the sol with definite amounts of the electrolyte and distilled water to keep the total volume 10 ml. The time of aggregation of the sol to a grain size which can be checked by Whatman filter paper No. 44 was determined as in part I (10). Plotting the inverse of the time of coagulation ( $1/t$ ) against the concentration of the electrolyte and extrapolating the curve to  $1/t = 0$ , the amount of the electrolyte required to coagulate the sol in infinite time was determined from the intercept of the curve on the axis representing concentration. The amount of the electrolyte for coagulating the sol of one third concentration was taken as 100%, and the percentage of the electrolyte for the higher sol concentrations were determined. The amount of the electrolyte for one hour of coagulation was also determined graphically and the results are given in tables I and II.

TABLE I

Coagulation values of the electrolytes in mM/litre in the mixed solution

for infinite time at  $(30 \pm 0.1)^\circ\text{C}$

Sol	KNO <sub>3</sub>		Ba (NO <sub>3</sub> ) <sub>2</sub>		Al (NO <sub>3</sub> ) <sub>3</sub>	
		%		%		%
A	65	118	1.30	130	0.0220	200
A/2	60	109	1.10	110	0.0140	127
A/3	55	100	1.00	100	0.0110	100
B	88	116	1.35	129	0.0200	190
B/2	80	105	1.15	110	0.0130	124
B/3	76	100	1.05	100	0.0105	100
C	95	113	1.48	132	0.0196	206
C/2	88	104	1.22	109	0.0125	132
C/3	84	100	1.12	100	0.0095	100
D	85	99	1.44	125	0.0178	209
D/2	88	102	1.25	109	0.0120	141
D/3	86	100	1.15	100	0.0085	100
E	80	111	1.40	127	0.0158	203
E/2	75	104	1.20	109	0.0105	135
E/3	72	100	1.10	100	0.0078	100

TABLE II

Sol	Coagulation values of the electrolytes in mM/litre in the mixed solution for one hour of observation at $(30 \pm 0.1)^\circ\text{C}$					
	KNO <sub>3</sub>		Ba (NO <sub>3</sub> ) <sub>2</sub>		Al (NO <sub>3</sub> ) <sub>3</sub>	
A	133.5	109	2.07	104	0.0275	187
A/2	129.5	105	2.03	102	0.0148	125
A/3	123.0	100	1.99	100	0.0147	100
B	146.5	107	2.20	106	0.0245	173
B/2	145.5	106	2.15	103	0.0172	121
B/3	137.0	100	2.08	100	0.0142	100
C	151.0	103	2.28	107	0.0236	186
C/2	149.0	102	2.20	103	0.0167	131
C/3	146.0	100	2.14	100	0.0127	100
D	156.5	104	2.35	107	0.0227	197
D/2	153.0	102	2.28	104	0.0156	136
D/3	150.0	100	2.20	100	0.0115	100
E	145.5	109	2.15	104	0.0183	183
E/2	140.0	104	2.10	102	0.0133	133
E/3	134.0	100	2.06	100	0.0100	100

The adsorption of the iodide ions in different sol samples was estimated by measuring the potential developed on the spiral Ag(s), AgI(s), I<sup>-</sup> electrode prepared by the method of Mirnik and Tezak (7) at 25°C against a decinormal calomel electrode. Liquid junction potential was eliminated by using saturated ammonium nitrate solution.

The e. m. f. of Ag(s), AgI(s), I<sup>-</sup> electrode is given by

$$E = E^\circ_{\text{Ag/AgI}} - \frac{2.303}{F} \frac{RT}{\log a_I} \quad \dots(1)$$

where  $E^\circ_{\text{Ag/AgI}}$  is the standard electrode potential of the composite Ag/AgI electrode, the value of which is - 0.1522 volt at 25°C and  $a_I^-$  is the activity of the iodide ions in solution. The value of  $a_I^-$  being known the concentration of the free iodide ions can be calculated by considering the ionic strengths of the electrolytes in solution. As the unadsorbed iodide ion concentration is low in comparison with the concentration of potassium nitrate in the sol, activity coefficient for iodide ions

in the sol was calculated by considering the ionic strengths of potassium and nitrate ions only. It needs to be stated here that the variations that will be caused in the value of the activity coefficient of iodide ion by taking into consideration the concentration of this ion in the sol will be insignificant when compared to the value calculated for the ionic strengths which affect the activity of the iodide ions. From the concentration of the free iodide ions thus obtained and also knowing the excess of potassium iodide added in preparing the sol, the amount of iodide ions adsorbed per gram of silver iodide was determined. Plotting  $-\log x/m$  against  $-\log C$ , a straight

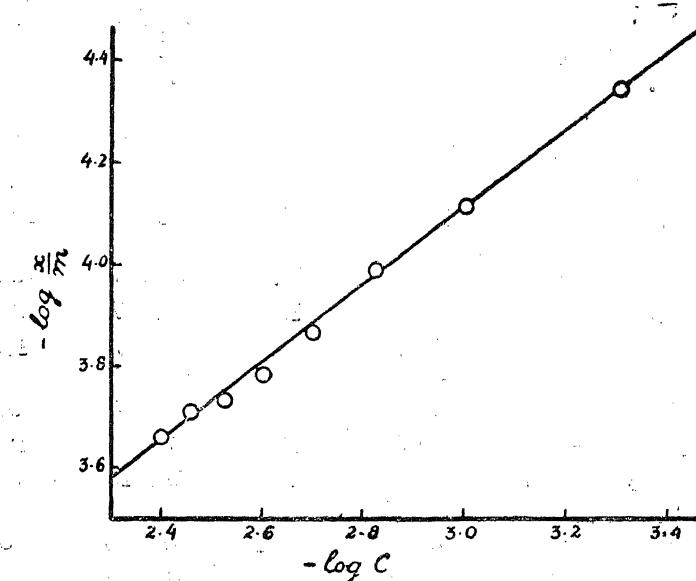


Fig. 1 Adsorption isotherm for iodide ions on colloidal silver iodide.

line is obtained (fig. 1), showing that this adsorption follows the Freundlich isotherm, which is

$$\log x/m = \log k + n \log C \quad \dots (2)$$

where the symbols have their usual significance. The values of  $n$  and  $k$  were also calculated and the results are given in table IV

TABLE III

Sol	Time of coagulation (hr.)	Amount of electrolyte in mM/litre in the mixed solution at $(30 \pm 0.1)^\circ C$		
		KNO <sub>3</sub>	Ba(NO <sub>3</sub> ) <sub>2</sub>	Al (NO <sub>3</sub> ) <sub>3</sub>
C	1	151	2.28	0.0236
C/2	2	133	1.97	0.0149
C/3	3	120	1.71	0.0108

TABLE IV

Amount of silver iodide in each sol = 0.02 gram mole per litre  
 Potassium nitrate present in each sol = 0.02 gram mole per litre  
 Temperature = 25°C

Sol no.	Excess of iodide ions in gram ion per litre of the sol = C	E. M. F. in volt against 0.1 N calomel electrode	$a_{I^-} \times 10^6$	Concentration of free iodide ions in gram ion per litre of the sol $\times 10^6$	Gram ions of iodide adsorbed per gram of silver iodide $\times 10^8$ $x/m \times 10^8$
1.	0.0005	0.2745	244	287	4535
2.	0.0010	0.2950	542	638	7707
3.	0.0015	0.3070	865	1018	10260
4.	0.0020	0.3145	1159	1364	13540
5.	0.0025	0.3205	1466	1726	16470
6.	0.0030	0.3260	1811	2131	18500
7.	0.0035	0.3310	2198	2586	19450
8.	0.0040	0.3345	2523	2969	21950

$$n = 0.77; k = 0.0158$$

#### RESULTS AND DISCUSSION

Tables I and II show that the amounts of the electrolytes with monovalent, bivalent and trivalent cations required to coagulate the negatively charged silver iodide sols decrease as the sols are diluted and Burton Bishop rule is not followed. As the concentration of the stabilising electrolyte potassium iodide is increased in the sols they become more stable towards the electrolytes potassium nitrate and barium nitrate and the sols have a tendency to obey Burton Bishop rule. As the time of observation for coagulation is increased the variation from the rule becomes more significant. It appears that as the factor of time is eliminated the sols show unstability with dilution but in any case the effect of iodide ions in controlling the applicability of Burton-Bishop rule is observable. Thus when observations are taken for infinite time for the sol D containing 0.0060 gram ions per litre of iodide in excess, the concentration of potassium nitrate required to coagulate the sols of various dilutions is practically constant.

According to Smoluchowski (8), as has pointed out by Kruyt and van der Spek (*loc cit*), the amount of an electrolyte required to coagulate the sols of different concentrations should be the same when the time of observation for the sol C/2 is increased two folds and the sol C/3 three folds of the time required to coagulate the sol C. The above can be concluded if we assume that (i) the charge on the colloidal particles remains to be the same on dilution, (ii) the charge neutralization on the colloidal particles is instantaneous and that the extent of the

charge neutralization is proportional to the concentration of the electrolyte added and that (iii) the coagulation is observed after a definite aggregation of the colloidal particles has been reached such that they attain a size which is checked by the pores of the filter paper. The amounts of electrolytes required to coagulate the sols C/2 and C/3 in two and three hours are obtained from the plots of  $1/t$  and concentration of the electrolyte. These are recorded in table III. It is seen here that in all the cases including the monovalent potassium ions from potassium nitrate the concentrations of the electrolytes required to coagulate the sols C/2 and C/3 decreases and do not remain constant.

We have already shown that the adsorption of the iodide ions follow Freundlich adsorption isotherm and necessarily when the sol is diluted the potassium iodide concentration becomes less with the consequence that the adsorption of the iodide ions per gram of silver iodide dispersed decreases leading to the decrease in electric charge on the colloidal particles. Thus desorption of the stabilising ion from the colloidal surface on diluting the sol is also a predominating factor for determining the stability of the sol on dilution.

Our results further show that for the electrolytes potassium nitrate and barium nitrate the stability of silver iodide sol increases as the iodide ion present in excess increases in amount. However, after a certain concentration of potassium iodide (See sol E) the sol becomes unstable with respect to these electrolytes, because the effect of the oppositely charged ion potassium present with the stabilising ion iodide becomes significant.

The effect of aluminium ions is, however, different. In this case the coagulating values decrease with the increasing concentration of free potassium iodide present in the sols. Kruyt (6) explains this from the view point related with the surface property of the dispersed particles, which is not easily understandable. If we assume that besides the electrostatic attraction of  $Al^{+++}$  by the negatively dispersed particles, the aluminium ions are also highly adsorbed it is possible to explain the result.

#### CONCLUSION

The stability of a sol on dilution is related to the nature of the coagulating electrolyte and the relative adsorption of the oppositely and similarly charged ions as has been pointed out by Ghosh and Dhar. In this paper it has been shown that the desorption of the stabilising ions by diluting the sols also plays a significant rôle.

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CERTAIN RULES AND RECURRENCE RELATIONS FOR  
MEIJER-LAPLACE TRANSFORM

By

V. M. BHISE

*Department of Mathematics, G. S. Technological Institute, Indore (M. P.)*

[Received on 23rd January, 1962]

1. A generalization of the classical Laplace transform

$$(1.1) \quad \phi(p) = p \int_0^\infty e^{-pt} \cdot f(t) dt$$

has been introduced by the author (1, p. 57) in the form

$$(1.2) \quad \phi(p) = p \int_0^\infty G_{m,m+1}^{m+1,0} \left( pt \left| \begin{matrix} \eta_1 + \alpha_1, \dots, \eta_m + \alpha_m \\ \eta_1, \dots, \eta_m, \rho \end{matrix} \right. \right) f(t) dt.$$

which reduces to (1.1) on putting  $\alpha_j = 0, j = 1, 2, \dots, m; \rho = 0$ . We shall call (1.2) Meijer-Laplace transform and denote it symbolically by

$$\phi \left( p \left| \begin{matrix} \alpha_1, \dots, \alpha_m \\ \eta_1, \dots, \eta_m, \rho \end{matrix} \right. \right) = G \left[ f(t) ; \left| \begin{matrix} \alpha_1, \dots, \alpha_m \\ \eta_1, \dots, \eta_m, \rho \end{matrix} \right. \right]$$

or briefly by  $\phi(p : \alpha_m, \eta_m, \rho) = G[f(t); \alpha_m, \eta_m, \rho]$

(i) With  $\alpha_i = 0, i = 1, 2, \dots, m-1; \alpha_m = \frac{1}{2} - m - k; \eta_m = 2m$  and  $\rho = 0$ , we get (1.2) reduced to Verma's transform (17, p. 209)

$$(1.3) \quad \phi(p) = p \int_0^\infty (pt)^{m-\frac{1}{2}} e^{-\frac{1}{2}pt} W_{k,m}(pt) f(t) dt.$$

We denote (1.3) symbolically by

$$\phi(p : k, m) = W[f(t); k, m]$$

(ii) With  $\alpha_i = 0, i = 1, 2, \dots, m-1; \alpha_m = -m-k; \eta_m = m-k$  and  $\rho = -m-k$ , we get (1.2) reduced to Meijer transform (12, p. 730)

$$(1.4) \quad \phi(p) = p \int_0^\infty (pt)^{-k-\frac{1}{2}} e^{-\frac{1}{2}pt} W_{k+\frac{1}{2}, m}(pt) f(t) dt$$

We denote (1.4) symbolically by

$$f(t) \xrightarrow[m]{k+\frac{1}{2}} \phi(p)$$

2. In this paper we have given certain rules of Meijer-Laplace transform with the help of the properties (2) of G-function,

$$(2.1) \quad \frac{d^n}{dx^n} \left[ x^{\alpha_r - 1} G_{p,q}^{l,u} \left( \frac{\beta}{x} \mid a_1, \dots, a_r, \dots, a_p \mid b_1, \dots, b_q \right) \right]$$

$$= x^{-1-n+\alpha_r} (-1)^n G_{p,q}^{l,u} \left( \frac{\beta}{x} \mid a_1, \dots, a_r - n, \dots, a_p \mid b_1, \dots, b_q \right)$$

where  $(-1)^n$  is omitted when  $r > u$ , and

$$(2.2) \quad \left( -x^2 \frac{d}{dx} \right)^n \left[ x^{1-\alpha_r} G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, a_r, \dots, a_p \mid b_1, \dots, b_q \right) \right]$$

$$= x^{1+n-\alpha_r} G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, a_r - n, \dots, a_p \mid b_1, \dots, b_q \right)$$

which is same as (2.1) with  $x$  replaced by  $\frac{1}{x}$ , and

$$(2.3) \quad \frac{d^n}{dx^n} \left[ x^{-b_r} G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, a_p \mid b_1, \dots, b_r, \dots, b_q \right) \right] = (-1)^n x^{-b_r - n} \cdot$$

$$\times G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, b_r + n, \dots, a_p \mid b_1, \dots, b_r, \dots, b_q \right)$$

where  $(-1)^n$  is omitted when  $r > l$ . From (2.3) we also have

$$(2.4) \quad \int x^{-b_r} G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, a_p \mid b_1, \dots, b_r, \dots, b_q \right) dx = -x^{-b_r + 1}$$

$$G_{p,q}^{l,u} \left( \beta x \mid a_1, \dots, b_r - 1, \dots, a_p \mid b_1, \dots, b_r, \dots, b_q \right)$$

where  $r \leq l$ .

We have given applications of some of the rules and have also derived some interesting recurrence relations for the Meijer-Laplace transform.

3. We give below some of the rules for the generalized Laplace-transform, which hold subject to certain conditions. These can be established by proceeding on the same lines as given by Bose (5, p. 19) in case of Whittaker transform.

(I) If  $G [f(t); \alpha_m, \eta_m, \rho] = \phi(p; \alpha_m, \eta_m, \rho)$  then

$$(i) G [f(at); \alpha_m, \eta_m, \rho] = \phi \left( \frac{p}{a}; \alpha_m, \eta_m, \rho \right) \quad (R. 1)$$

$$(ii) G \left[ \left( t \frac{d}{dt} \right)^n f(t); \alpha_m, \eta_m, \rho \right] = \left( -p \frac{d}{dp} \right)^n \phi(p; \alpha_m, \eta_m, \rho) \quad (R. 2)$$

$$(iii) G \left[ \int_0^t f(x) \cdot \frac{dx}{x} ; \alpha_m, \eta_m, \rho \right] = \int_p^\infty \phi(x; \alpha_m, \eta_m, \rho) \frac{dx}{x} \quad (R. 3)$$

$$(iv) G \left[ \int_t^\infty f(x) \frac{dx}{x} ; \alpha_m, \eta_m, \rho \right] = \int_p^\infty \phi(x; \alpha_m, \eta_m, \rho) \frac{dx}{x} \quad (R. 4)$$

$$(v) \int_0^\infty \phi(p; \alpha_m, \eta_m, \rho) \frac{dp}{p^\lambda} = \sum_{j=1}^m \frac{\frac{\pi}{\Gamma(\eta_j - \lambda + 2)} \Gamma(\rho - \lambda + 2)}{\frac{\pi}{\Gamma(\eta_j + \alpha_j - \lambda + 2)}} \int_0^\infty t^{\lambda - 2} \cdot f(t) dt \quad (R. 5)$$

(II) If  $G[f_i(t); \alpha_m, \eta_m, \rho] = \phi_i(p; \alpha_m, \eta_m, \rho)$ ,  $i=1, 2$ , then

$$\int_0^\infty f_1(t) \phi_2(t; \alpha_m, \eta_m, \rho) \frac{dt}{t} = \int_0^\infty f_2(t) \phi_1(t; \alpha_m, \eta_m, \rho) \frac{dt}{t} \quad (R. 6)$$

(III) If  $G[f_i(t); \alpha_m, \eta_m, \rho] = \phi_i(p; \alpha_m, \eta_m, \rho)$ ,  $i=1, 2, \dots, n$ , then

$$G \left[ \sum_{i=1}^n f_i(t); \alpha_m, \eta_m, \rho \right] = \sum_{i=1}^n \phi_i(p; \alpha_m, \eta_m, \rho) \quad (R. 7)$$

4. In this section we give seven rules for the generalized transform. Three of these rules are the recurrence relations for the Meijer-Laplace transform. On specialising the parameters these yield many known and unknown recurrence relations for the Verma's transform and Meijer's transform.

$$\text{If } G[f(t); \alpha_m, \eta_m, \rho] = \phi(p; \alpha_m, \eta_m, \rho)$$

and if the integrals involved are convergent, then

$$(i) G \left[ t^{-\eta} \int_0^t \int_0^x \dots \int_0^x x^{\eta - N} f(x) (dx)^N ; \alpha_1, \dots, \alpha_m ; \eta_1, \dots, \eta_{m-1}, \eta, \rho \right] = \phi(p; \alpha_1, \dots, \alpha_{m-1}, \alpha_m + N; \eta_1, \dots, \eta_{m-1}, \eta - N, \rho) \quad (R. 8)$$

$$\text{provided } \left[ t^{-\eta - j + 1} G_{m, m+1}^{m+1, 0} \left( pt \mid \eta_1 + \alpha_1, \dots, \eta_{m-1} + \alpha_{m-1}, \eta + \alpha_m ; \eta_1, \dots, \eta_{m-1}, \eta + j - 1, \rho \right) \right]$$

$$\times \int_0^t \int_0^x \dots \int_0^x x^{\eta} f(x) (dx)^j \int_0^\infty \dots \int_0^\infty$$

are all zero,

$$(ii) G \left[ t^{-r} \int_0^t \int_0^x \dots \int_0^x x^{r-N} f(x) (dx)^N ; \alpha_1, \dots, \alpha_m ; \eta_1, \dots, \eta_m, r \right] = \phi(p; \alpha_1, \dots, \alpha_m ; \eta_1, \dots, \eta_m, r - N) \quad (R. 9)$$

provided  $\left[ t^{-r-j+1} G_{m,m+1}^{m+1,0} (pt \mid \eta_1 + \alpha_1, \dots, \eta_m + \alpha_m, \eta_1, \dots, \eta_m, r+j-1) \int_0^t \int_0^x \dots \int_0^x x^r f(x) dx^{m-1} \right]_0^\infty$ ,

$$j = 2, \dots, N$$

are all zero.

$$(iii) G \left[ t^{-\eta - a - 1} \int_0^t x^{\eta + a} f(x) dx ; \eta_1, \dots, \eta_{m-1}, \eta, \rho \right] = \phi \left( p : \eta_1, \dots, \eta_{m-1}, \eta, \rho \right) \quad (R. 10)$$

provided  $\left[ t^{1-\eta-a} G_{m,m+1}^{m+1,0} (pt \mid \eta_1 + \alpha_1, \dots, \eta_{m-1} + \alpha_{m-1}, \eta + a, \eta_1, \dots, \eta_{m-1}, \eta, \rho) \int_0^t x^{\eta + a - 1} f(x) dx \right]_0^\infty$

is zero,

$$(iv) G \left[ t^{-\eta} \frac{d^N}{dt^N} \left\{ t^{\eta+N} f(t) \right\} ; \eta_1, \dots, \eta_{m-1}, \eta, \rho \right] = \phi \left( p : \eta_1, \dots, \eta_{m-1}, \eta + N, \rho \right) \quad (R. 11)$$

provided  $t^{-\eta+j} G_{m,m+1}^{m+1,0} (pt \mid \eta_1 + \alpha_1, \dots, \eta + \alpha_m, \eta_1, \dots, \eta_{m-1}, \eta - j, \rho) \frac{d^j}{dt^{j-1}} \left\{ t^{\eta} f(t) \right\} \right], j = 1, 2, \dots, N$

are all zero.

(R. 8) and (R. 9) can be derived from (1.2) by repeated integration by parts, using (2.3) and changing the parameters suitably. Again from (1.2), integrating by parts, using (2.2) and with suitable change in parameters yield (R. 10)). Repeated integration by parts of the right hand side of (1.2) with the help of (2.4) and replacing  $\alpha_m, \eta$  by  $\alpha_m - N, \eta + N$  we obtain (R.11).

Now we give some interesting recurrence relations of Meijer-Laplace transform. If  $G[f(t); \alpha_m, \eta_m, \rho] = \phi(p : \alpha_m, \eta_m, \rho)$  and the integrals involved are convergent, then

$$(i) \frac{d^N}{dp^N} \left[ p^{-\eta_m - 1} \phi(p : \eta_1, \dots, \eta_m, \rho) \right] = (-1)^N p^{-\eta_m - N - 1} \phi(p : \eta_1, \dots, \eta_{m-1}, \eta_m + N, \rho) \quad (R. 12)$$

$$(ii) \frac{d^N}{dp^N} \left[ p^{-\rho - 1} \phi(p : \eta_1, \dots, \eta_m, \rho) \right] = (-1)^N p^{-\rho - N - 1} \times \phi(p : \eta_1, \dots, \eta_m, \rho \times N) \quad (R. 13)$$

$$(iii) \left( -p^2 \frac{d}{dp} \right)^N \left[ p^{-\eta_m - \alpha_m} \phi \left( p : \frac{\alpha_1, \dots, \alpha_m}{\eta_1, \dots, \eta_m, \rho} \right) \right] = p^{-\eta_m - \alpha_m - N} \times \phi \left( p : \frac{\alpha_1, \dots, \alpha_{m-1}, \alpha_m - N}{\eta_1, \dots, \eta_m, \rho} \right) \quad (R.14)$$

we obtain (R.12), (R.13) on multiplying both sides of (1.2) by  $p^{-\eta_1 - 1}, p^{-\rho - 1}$  and then differentiating  $N$  times with respect to  $p$  by the help of (2.3). Again multiplying

both sides of (1.2) by  $p^{-\eta_m - \alpha_m}$ , operating  $\left( -p^2 \frac{d}{dp} \right)^N$  on both sides, and using (2.2) yields (R. 14).

(4a) Putting  $\alpha_i = 0, i = 1, 2, \dots, m-1; \alpha_m = \frac{1}{2} - m - k; \eta_m = 2m; \rho = 0$  using (8, p. 375) and taking  $f(t) = t^\lambda F(t)$  in (R. 12), (R. 13) and (R. 14) we have the following recurrence relations for the Verma's transform.

If  $W[t^\lambda F(t); k, m] = \phi(p; k, m; \lambda)$ , then

$$(4.1) \frac{d^N}{dp^N} \left[ p^{-2m-1} \phi(p; k, m; \lambda) \right] = (-1)^N p^{-2m-N-1} \times \phi(p; k + \frac{N}{2}, m + \frac{N}{2}; \lambda)$$

$$(4.2) \frac{d^N}{dp^N} \left[ p^{-1} \phi(p; k, m; \lambda) \right] = (-1)^N p^{-1} \phi(p; k + \frac{N}{2}, m - \frac{N}{2}, \lambda + N)$$

which is a known result (14, p. 391), and

$$(4.3) \left( -p^2 \frac{d}{dp} \right)^N \left[ p^{-\frac{1}{2}-m+k} \phi(p; k, m; \lambda) \right] = p^{-\frac{1}{2}-m+k+N} \phi(p; k + N, m; \lambda)$$

with  $N=1$  we have these relations in the form,

$$(4.4) p \frac{d}{dp} \phi(p; k, m; \lambda) = (2m+1) \phi(p; k, m; \lambda) - \phi(p; k + \frac{1}{2}, m + \frac{1}{2}; \lambda)$$

$$(4.5) p \frac{d}{dp} \phi(p; k, m; \lambda) = \phi(p; k, m; \lambda) - p \phi(p; k + \frac{1}{2}, m - \frac{1}{2}; \lambda + 1)$$

which has been obtained by Roop Narain (15, p. 29), and

$$(4.6) p \frac{d}{dp} \phi(p; k, m; \lambda) = (\frac{1}{2} + m - k) \phi(p; k, m; \lambda) - \phi(p; k + 1, m; \lambda)$$

We shall now obtain many known relations by using (4.4), (4.5) and (4.6).

Subtraction of (4.5) and (4.6) gives

$$(4.7) \phi(p; k+1, m; \lambda) = p \phi(p; k+\frac{1}{2}, m-\frac{1}{2}; \lambda+1) + (-\frac{1}{2}+m-k) \phi(p; k, m; \lambda)$$

With  $k$  by  $k-1$ , we have a known result (14, p. 391).

Subtraction of (4.4) and (4.6) gives,

$$(4.8) (-\frac{1}{2}-m-k) \phi(p; k, m; \lambda) = \phi(p; k+1, m; \lambda) - \phi(p; k+\frac{1}{2}, m+\frac{1}{2}; \lambda)$$

With  $k$  replaced by  $k-1$  we have other known result (14, p. 391).

Finally, the subtraction of (4.4) and (4.5) yields,

$$(4.9) 2m \phi(p; k, m; \lambda) = \phi(p; k+\frac{1}{2}, m+\frac{1}{2}; \lambda) - p \phi(p; k+\frac{1}{2}, m-\frac{1}{2}; \lambda+1)$$

In (4.8) replace  $\lambda, m$  by  $\lambda+1, m-1$  and multiply both sides by  $p$ . Now, adding (4.9) with  $k+\frac{1}{2}, m-\frac{1}{2}$  for  $k, m$  and using (4.7) we have a result by Rathie (14, p. 392). Subtract from this result with  $k$  replaced by  $k-1$ , the relation (4.9) with  $k, m$  replaced by  $k-\frac{1}{2}, m-\frac{1}{2}$ , to get a relation by Bhonsle (4, p. 120).

Multiply both sides of (4.8) by  $p$ , replacing  $\lambda, k, m$  by  $\lambda+1, k-\frac{1}{2}, m-\frac{1}{2}$ . Also, replace  $k$  by  $k-1$  in (4.7) and multiply both sides by  $m+k-\frac{1}{2}$ . Subtraction of these two results yields another known relation by Bhonsle (4, p. 120).

(4b) Putting  $a_i = 0, i=1, 2, \dots, m-1; \alpha_m = -m-k; \eta_m = m-k; \rho = -m-k$ , using (7, p. 216, 6) and taking  $f(t) = t^\lambda F(t)$  in (R.12), (R.13) and (R.14) we get the following recurrence relations for the Meijer's transform.

If  $t^\lambda F(t) \xrightarrow[m]{k} \phi_{k, m, \lambda}(p)$ , then

$$(4.10) \frac{d^N}{dp^N} \left[ p^{-m+k-1} \phi_{k+\frac{1}{2}, m, \lambda}(p) \right] = (-1)^N p^{-m+k-1} \times \phi_{k+\frac{N+1}{2}, m+\frac{N}{2}, \lambda+N}(p)$$

$$(4.11) \frac{d^N}{dp^N} \left[ p^{m+k-1} \phi_{k+\frac{1}{2}, m, \lambda}(p) \right] = (-1)^N p^{m+k-1} \times \phi_{k+\frac{N+1}{2}, m-\frac{N}{2}, \lambda+N}(p) \text{ and}$$

$$(4.12) \left( -p^2 \frac{d}{dp} \right)^N \left[ p^{2k} \phi_{k+\frac{1}{2}, m, \lambda}(p) \right] = p^{2m+2k} \phi_{k+\frac{2N+1}{2}, m, \lambda+N}(p)$$

With  $N=1$  these take the forms

$$(4.13) p \frac{d}{dp} \phi_{k+\frac{1}{2}, m, \lambda}(p) = (1+m-k) \phi_{k+\frac{1}{2}, m, \lambda}(p) - p \cdot \phi_{k+\frac{1}{2}, m+\frac{1}{2}, \lambda+1}(p),$$

$$(4.14) \quad p \cdot \frac{d}{dp} \phi_{k+\frac{1}{2}, m, \lambda}(p) = (1-m-k) \phi_{k+\frac{1}{2}, m, \lambda}(p) - p \cdot \phi_{k+1, m-\frac{1}{2}, \lambda+1}(p),$$

$$(4.15) \quad p \cdot \frac{d}{dp} \phi_{k+\frac{1}{2}, m, \lambda}(p) = -2k \phi_{k+\frac{1}{2}, m, \lambda}(p) - p \cdot \phi_{k+\frac{3}{2}, m, \lambda+1}(p)$$

With  $k = -\frac{1}{2}$  in (4.15), we obtain a result by Jain (9, p. 134).

In the subtraction of (4.13), (4.15) and of (4.14), (4.15), replace  $\lambda, k$  by  $\mu - 1, k - 1$ , to get recurrence relations due to Jaiswal (10)

5. In this section we have given the Meijer-Laplace transform of some functions. These will be required later on for illustrating the rules established in the previous sections.

Using a known integral (16, p. 401), we obtain,

$$(5.1) \quad G \left[ t^{-n\lambda} \quad G_{\gamma, \delta}^{\alpha, \beta} \left( \left| \begin{array}{c} a_1, \dots, a_{\gamma} \\ b_1, \dots, b_{\delta} \end{array} \right. \right); \alpha_m, \eta_m, \rho \right]$$

$$= p^{n\lambda} \cdot (2\pi)^{\frac{1-n}{2}} \cdot n^{\rho - \sum_1^m \alpha_j - n\lambda + \frac{1}{2}} \cdot (2\pi)^{(1-s)(\alpha + \beta - \frac{1}{2}\nu - \frac{1}{2}\delta)} \cdot$$

$$\times \sum_{s=1}^{\delta} \sum_{i=1}^{\gamma} a_i + \frac{1}{2} \gamma - \frac{1}{2} \delta + 1$$

$$\times G_{sv + nm + n, s\delta + n}^{s\alpha, s\beta + nm + n} \left( \left| \begin{array}{c} \Delta(s, a_1), \dots, \Delta(s, a_{\beta}), \Delta(n, n\lambda - \eta_1), \\ \Delta(s, b_1), \dots, \Delta(s, b_{\alpha}), \Delta(n, n\lambda - \eta_1 - \alpha_1), \\ \dots, \Delta(n, n\lambda - \eta_m), \Delta(n, n\lambda - \rho), \Delta(s, a_{\beta+1}), \dots, \Delta(s, a_{\gamma}), \\ \dots, \Delta(n, n\lambda - \eta_m - \alpha_m), \Delta(s, b_{\alpha+1}), \dots, \Delta(s, b_{\delta}) \end{array} \right. \right)$$

where  $n, s$  are positive integers and  $\Delta(m, a)$  stands for the set of parameters

$$\frac{a}{m}, \frac{a+1}{m}, \frac{a+2}{m}, \dots, \frac{a+m-1}{m}$$

$0 \leq \alpha \leq \delta, 0 \leq \beta \leq \gamma, 2(\alpha + \beta) > \gamma + \delta, |\arg z| < (\alpha + \beta - \frac{1}{2}\gamma - \frac{1}{2}\delta)\pi, |\arg p| < \pi/2,$

$$R(\min \eta_j, \rho + \frac{n}{s} \min b_j) > n R(\lambda) - 1 > R(\frac{n}{s} a_i - \frac{n}{s} - 1), i = 1, 2, \dots, m;$$

$$j = 1, 2, \dots, \alpha; f = 1, 2, \dots, \beta.$$

$$(i) \text{ As } G_{0,1}^{1,0}(\frac{1}{2}t^2/0) = e^{-\frac{1}{2}t^2}, \text{ putting } \alpha = 1 = \delta, \beta = 0 = \gamma, n = 2, s = 1,$$

$z = \frac{1}{2}, \lambda = 0, b_1 = 0$  in (5.1) we have,

$$(5.2) \quad G \left[ e^{-\frac{1}{2} t^2} ; \alpha_m, \eta_m, \rho \right] = \frac{2^{\rho - \sum_{j=1}^m \alpha_j}}{\sqrt{\pi}}.$$

$$\times G_{2m+2, 2m+1}^{1, 2m+2} \left( \frac{2}{p^2} \left| \begin{array}{c} -\eta_1, -\eta_1+1, \dots, -\eta_m, -\eta_m+1, -\rho, -\rho+1 \\ 0, -\eta_1-\alpha_1, -\eta_1-\alpha_1+1, \dots, -\eta_m-\alpha_m, -\eta_m-\alpha_m+1 \end{array} \right. \right)$$

$$R(p) > 0, R(\min_j \eta_j, \rho) > -1, j=1, 2, \dots, m.$$

With  $\alpha_j = 0, j=1, 2, \dots, m; \rho = 0$  we get a known result (8, p. 146, 21).

(ii) Putting  $\alpha-1=\delta, \beta=0=\gamma, n=1=s, z=\beta, \lambda=-\nu, b_1=0$  in (5.1) and using (7, p. 209, 9) we have,

$$(5.3) \quad G \left[ t^\nu e^{-\beta t} ; \alpha_m, \eta_m, \rho \right] = p^\rho \beta^{-\nu-1}$$

$$\times G_{m+1, m+1}^{m+1, 1} \left( \frac{p}{\beta} \left| \begin{array}{c} -\nu, \eta_1+\alpha_1, \dots, \eta_m+\alpha_m \\ \eta_1, \dots, \eta_m, \rho \end{array} \right. \right)$$

$$R(p) > 0, R(\eta_j + \nu) > -1, j=1, 2, \dots, m; R(\rho + \nu) > -1, R(p + \beta) > 0, |\arg \beta| < \pi/2.$$

(iii) We now consider the integro-exponential function  $E_\nu(t)$  defined by Busbridge (6). This function is used in problems connected with the radiative equilibrium of stellar atmospheres and in problems of neutron diffusion. We have from Bhonsle (3, p. 157) the relation

$$E_\nu(t) = e^{-\frac{1}{2} t} W_{-\frac{1}{2} \nu, \frac{1}{2} - \frac{1}{2} \nu}(t) \cdot t^{\frac{1}{2} \nu - 1}$$

Using (7, p. 216, 6) we get,

$$t^\sigma E_\nu(t^n | s) = G_{1,2}^{2,0} \left( t^n | s \left| \begin{array}{c} \frac{s}{n} \sigma + \nu \\ \frac{s}{n} \sigma, \frac{s}{n} \sigma + \nu - 1 \end{array} \right. \right)$$

With this relation, we obtain, from (5.1), the correspondences

$$(5.4) \quad G \left[ t^\sigma E_\nu(t^n | s) ; \alpha_m, \eta_m, \rho \right] = (2\pi)^{\frac{2-n-s}{2}} \cdot n^{\rho - \sum_{j=1}^m \alpha_j + \frac{1}{2}} \cdot s^{\frac{s\sigma}{n} - \frac{1}{2}}$$

$$\times G_{s+nm+n, 2s+nm}^{2s, nm+n} \left( \frac{n^n}{s^s p^n} \left| \begin{array}{c} \Delta(n, -\eta_1), \dots, \Delta(n, -\eta_m), \\ \Delta(s, \frac{s\sigma}{n}), \Delta(s, \frac{s\sigma}{n} + \nu - 1), \end{array} \right. \right)$$

$$\dots, \Delta(n, -\rho), \Delta(s, \frac{s\sigma}{n} + \nu)$$

$$\dots, \Delta(n, -\eta_1 - \alpha_1), \dots, \Delta(n, -\eta_m - \alpha_m)$$

where  $n, s$  are positive integers,  $R(p) > 0$ ,  $R(\min \eta_j, \rho + \sigma) > -1$ ,

$$R[\min \eta_j, \rho + \sigma + \frac{n}{s}(v-1)] > -1, j=1, 2, \dots, n.$$

Putting  $\alpha_j=0, j=1, 2, \dots, m$ ;  $\rho=0$  we get a known result by Busbridge (6).

(iv) Lastly we have, because  $t^\mu J_\nu(\beta t) = \left(\frac{2}{\beta}\right)^\mu \cdot G_{0,2}^{1,0} \left(\frac{\beta^2 t^2}{4} \middle| \frac{\mu+v}{2}, \frac{\mu+v}{2}\right)$

$$(5.5) \quad G \left[ t^\mu J_\nu(\beta t); \alpha_m, \eta_m, \rho \right] = \frac{2^{\rho - \sum_1^m \alpha_j + \mu}}{\beta^\mu \sqrt{\pi}} \times G_{2m+2, 2m+2}^{1, 2m+2} \left( \frac{\beta^2}{p^2} \middle| \frac{-\eta_1}{2}, \frac{-\eta_1+1}{2}, \dots, \frac{-\eta_m}{2}, \frac{-\eta_m+1}{2}, \frac{-\rho}{2}, \frac{-\rho+1}{2} \right) \times G_{2m+2, 2m+2}^{1, 2m+2} \left( \frac{\beta^2}{p^2} \middle| \frac{\mu+v}{2}, \frac{-\eta_1-\alpha_1}{2}, \frac{-\eta_1-\alpha_1+1}{2}, \dots, \frac{-\eta_m-\alpha_m}{2}, \frac{-\eta_m-\alpha_m+1}{2}, \frac{\mu-v}{2} \right)$$

$R(p) > 0$ ,  $R(\min \eta_j, \rho + \mu + v) > -1, j=1, 2, \dots, m$ ;  $|p| > |\beta|$

When  $\alpha_j = 0, j=1, 2, \dots, m-1$ ;  $\alpha_m = \frac{1}{2} - m - k$ ;  $\eta_m = 2m$ ;  $\rho=0$ , (5.3), (5.5) reduce to known results (14, p. 382), (15, p. 31).

6. Now we give applications of some of the rules established in previous sections.

(a) Applying (R.2) to (5.4) we have

$$G \left[ t \frac{d}{dt} \left\{ t^\sigma E_\nu \left( t^{n/s} \right) \right\}; \alpha_m, \eta_m, \rho \right] = - (2\pi) \frac{2-n-s}{2} \frac{\rho - \sum_1^m \alpha_j + \frac{1}{2}}{n} \frac{s\sigma}{s - \frac{1}{2}} \times p \frac{d}{dp} G_{s+nm+n, 2s+nm}^{2s, nm+n} \left( \frac{n^n}{s^n p^n} \middle| \begin{array}{l} \Delta(n, -\eta_1), \dots, \Delta(n, -\eta_m), \\ \Delta(s, \frac{s\sigma}{n}), \Delta(s, \frac{s\sigma}{n} + v - 1), \end{array} \right. \dots, \Delta(n, -\rho), \Delta(s, \frac{s\sigma}{n} + v) \left. \dots, \Delta(n, -\eta_1 - \alpha_1), \dots, \Delta(n, -\eta_m - \alpha_m) \right)$$

Replacing  $p^{-n}$  by  $\rho$ , applying the formula (2), we obtain in terms of  $p$

$$(6.1) \quad G \left[ t \frac{d}{dp} \left\{ t^\sigma E_\nu \left( t^{\frac{n}{s}} \right) \right\}; \alpha_m, \eta_m, \rho \right] = (2\pi) \frac{2-n-s}{2} \frac{m}{n} \rho - \sum_1^m \alpha_j + \frac{1}{2} \cdot \frac{s\sigma}{s - \frac{1}{2}} \text{ multiplied by}$$

$$\times \left[ \sigma G_{s+nm+n, 2s+nm}^{2s, nm+n} \left( \frac{n^n}{s^n p^n} \middle| \begin{array}{l} \Delta(n, -\eta_1), \dots, \Delta(n, -\eta_m), \Delta(n, -\rho), \Delta(s, \frac{s\sigma}{n} + \nu) \\ \Delta(s, \frac{s\sigma}{n}), \Delta(s, \frac{s\sigma}{n} + \nu - 1), \Delta(n, -\eta_1 - \alpha_1), \dots, \\ \Delta(n, -\eta_m - \alpha_m) \end{array} \right) \right. \\ \left. G_{s+nm+n, 2s+nm}^{2s, nm+n} \left( \frac{n^n}{s^n p^n} \middle| \begin{array}{l} \Delta(n, -\eta_1), \dots, \Delta(n, -\eta_m), \Delta(n, -\rho), \Delta(s, \frac{s\sigma}{n} + \nu) \\ \Delta(s, \frac{s\sigma}{n} + 1), \Delta(s, \frac{s\sigma}{n} + \nu - 1), \Delta(n, -\eta_1 - \alpha_1), \dots, \\ \Delta(n, -\eta_m - \alpha_m) \end{array} \right) \right]$$

$$|\arg p| < \frac{\pi}{2}, R(\min \eta_j, \rho + \sigma) > -1, R[\min \eta_j, \rho + \frac{n}{s}(v-1)] > -1, j=1, 2, \dots, m.$$

Using the recurrence formulae (6, p. 178)

$$E_v'(t) = -E_{v-1}(t)$$

we obtain the relation

$$t \frac{d}{dt} [ t^\sigma E_v(t^{n/s}) ] = \sigma t^\sigma E_v(t^{n/s}) - \frac{n}{s} t^{\sigma+n/s} E_{v-1}(t^{n/s})$$

On applying (R.7) and (5.4) to the right hand side, we can verify (6.1).

(b) Applying (R.3) to (5.5) and using (7, p. 209,9), we obtain,

$$G \left[ \int_0^\infty t^{\mu-1} J_\nu(\beta t) dt ; \alpha_m, \eta_m, 0 \right] \\ = \frac{2^{\mu-\sum_1^m \alpha_j}}{\beta^\mu \sqrt{\pi}} \int_0^\infty G_{2m+2, 2m+2}^{2m+2, 1} \left( \frac{p^2}{\beta^2} \middle| \begin{array}{l} \frac{1}{2}(2-\mu-\nu), \frac{1}{2}(\eta_1+\alpha_1+1+\frac{1}{2}\pm\frac{1}{2}), \dots, \\ \frac{1}{2}(\eta_1+1+\frac{1}{2}\pm\frac{1}{2}), \dots, \dots, \dots, \\ \dots, \frac{1}{2}(\eta_m+\alpha_m+1+\frac{1}{2}\pm\frac{1}{2}), \frac{1}{2}(2-\mu+\nu) \\ \dots, \frac{1}{2}(\eta_m+1+\frac{1}{2}\pm\frac{1}{2}), 1, \frac{1}{2} \end{array} \right) \cdot \frac{dp}{p}$$

with the help of (2.4) we have,

$$(6.2) G \left[ \int_0^\infty t^{\mu-1} J_\nu(\beta t) dt ; \alpha_m, \eta_m, 0 \right] = \frac{2^{\mu-\sum \alpha_j-1}}{\beta^\mu \sqrt{\pi}} \\ \times G_{2m+2, 2m+2}^{2m+2, 1} \left( \frac{p^2}{\beta^2} \middle| \begin{array}{l} \frac{1}{2}(2-\mu-\nu), \frac{1}{2}(\eta_1+\alpha_1+1+\frac{1}{2}\pm\frac{1}{2}), \dots, \\ \frac{1}{2}(\eta_1+1+\frac{1}{2}\pm\frac{1}{2}), \dots, \dots, \dots, \\ \dots, \frac{1}{2}(\eta_m+\alpha_m+1+\frac{1}{2}\pm\frac{1}{2}), \frac{1}{2}(2-\mu+\nu) \\ \dots, \frac{1}{2}(\eta_m+1+\frac{1}{2}\pm\frac{1}{2}), 0, \frac{1}{2}. \end{array} \right)$$

$$R(\min \eta_j + \nu) > -1, j=1, 2, \dots, m; R(\mu + \nu) > 0, R(p + \beta) > 0$$

(i) With  $\beta = \frac{1}{a}$ ,  $\mu = 0$ ,  $\alpha_j = 0$ ,  $j = 1, 2, 3, \dots, m$ , using (8, p. 377) and (13, p. 70),

we get a known result (11, p. 365, 55).

(ii) Consider the Fresnel's integrals, defined by

$$s(x) = \frac{1}{2} \int_0^x J_{\frac{1}{2}}(x) dx, \quad e(x) = \frac{1}{2} \int_0^x J_{-\frac{1}{2}}(x) dx$$

$\beta = 1$ ,  $\mu = 1$ ,  $\nu = \frac{1}{2}$  yields,

$$(6.3) G[s(t); \alpha_m, \eta_m, o] = \frac{2 - \sum_{j=1}^m \alpha_j - 1}{\sqrt{\pi}}.$$

$$G_{2m+2, 2m+2}^{2m+2, 1} \left( p^2 \left| \begin{array}{l} \frac{1}{4}, \frac{1}{2}(\eta_1 + \alpha_1 + 1 + \frac{1}{2} \pm \frac{1}{2}), \dots, \frac{1}{2}(\eta_m + \alpha_m + 1 + \frac{1}{2} \pm \frac{1}{2}), \frac{3}{4} \\ \frac{1}{2}(\eta_1 + 1 + \frac{1}{2} \pm \frac{1}{2}), \dots, \frac{1}{2}(\eta_m + 1 + \frac{1}{2} \pm \frac{1}{2}), 0, \frac{1}{2} \end{array} \right. \right)$$

$$R \left( \min \eta_j + \frac{5}{2} \right) > 0, j=1, 2, \dots, m; R(p+1) > 0$$

(iii)  $\beta = 1$ ,  $\mu = 1$ ,  $\nu = -\frac{1}{2}$  yields,

$$(6.4) G[e(t); \alpha_m, \eta_m, o] = \frac{2 - \sum_{j=1}^m \alpha_j - 1}{\sqrt{\pi}}$$

$$\times G_{2m+2, 2m+2}^{2m+2, 1} \left( p^2 \left| \begin{array}{l} \frac{3}{4}, \frac{1}{2}(\eta_1 + \alpha_1 + 1 + \frac{1}{2} \pm \frac{1}{2}), \dots, \frac{1}{2}(\eta_m + \alpha_m + 1 + \frac{1}{2} \pm \frac{1}{2}), \frac{1}{4} \\ \frac{1}{2}(\eta_1 + 1 + \frac{1}{2} \pm \frac{1}{2}), \dots, \frac{1}{2}(\eta_m + 1 + \frac{1}{2} \pm \frac{1}{2}), 0, \frac{1}{2} \end{array} \right. \right)$$

$$R \left( \min \eta_j + \frac{3}{2} \right) > 0, j = 1, 2, \dots, m; R(p+1) > 0.$$

Putting  $\alpha_j=0, j=1, 2, \dots, m-1$ ;  $\alpha_m=\frac{1}{2}+m-k$ ;  $\eta_m=2m$ , (6.3) and (6.4) yield known results (15, p. 33).

(c) Again applying (R.8) to (5.4) we have,

$$(6.5) \quad G \left[ t^{-\eta} \int_0^t \int_0^x \dots \int_0^x x^{\sigma} - N + \eta E_{\nu} (dx^{n/s}) (dx)^N ; \frac{\alpha_1, \dots, \alpha_m}{\eta_1, \dots, \eta_{m-1}, \eta, \rho} \right]$$

$$= (2\pi)^{\frac{2-n-s}{2}} \cdot n^{\rho - \sum \alpha_j - N + \frac{1}{2}} s^{\frac{s\sigma}{n} - \frac{1}{2}}$$

$$\times G_{s+n, nm+n}^{2s, nm+n} \left( \frac{n^n}{p^n s^n} \left| \begin{array}{l} \Delta(n, -\eta_1), \dots, \Delta(n, -\eta_{m-1}), \Delta(n, -\eta+N), \\ \Delta(s, \frac{s\sigma}{n}), \Delta(s, \frac{s\sigma}{n} + \nu - 1), \Delta(n, -\eta_1 - \alpha_1), \dots, \\ \dots, \Delta(n, -\rho), \Delta(s, \frac{s\sigma}{n} + \nu) \\ \dots, \Delta(n, -\eta_{m-1} - \alpha_{m-1}), \Delta(n, -\eta - \alpha_m) \end{array} \right. \right)$$

where  $n, s$  are positive integers,  $|\arg p| < \pi/2$ ,  $R(\min \eta_j, \rho + \sigma) > -1$ ,

$$R[\min \eta_j, \rho + \sigma + \frac{n}{s}(\nu - 1)] > -1, \quad j=1, 2, \dots, m-1; \quad R(|\eta - N + \sigma|) > -1;$$

$$R[\eta - N + \sigma + \frac{n}{s}(\nu - 1)] > -1.$$

With  $\eta=0, \alpha_j=0, j=1, 2, \dots, m; \rho=0$  we have,

$$(6.6) \quad \int_0^t \int_0^x \dots \int_0^x x^{\sigma} - N E_{\nu} (x^{n/s}) (dx)^N = \frac{(2\pi)^{\frac{2-n-s}{2}} \cdot s^{\frac{s\sigma}{n} - \frac{1}{2}}}{n^{N - \frac{1}{2}}} \times G_{s+n, 2s}^{2s, n} \left( \frac{n^n}{p^n s^n} \left| \begin{array}{l} \Delta(n, N), \Delta(s, \frac{s\sigma}{n} + \nu) \\ \Delta(s, \frac{s\sigma}{n}), \Delta(s, \frac{s\sigma}{n} + \nu - 1) \end{array} \right. \right)$$

$$|\arg p| < \frac{\pi}{2}, \quad R(\sigma - N) > -1, \quad R[\sigma - N + \frac{n}{s}(\nu - 1)] > 0,$$

With  $n=s=1$  and using (8, p. 377) we get,

$$(6.7) \quad \int_0^t \int_0^x \cdots \int_0^z x^{\sigma-N} \cdot E_{\nu}(x) \cdot (dx)^N = \frac{\Gamma(\sigma-N+1) \Gamma(\sigma-N+\nu)}{\Gamma(\sigma-N+\nu+1) p^{N-1}} \cdot$$

$$+ {}_2F_1\left(\begin{matrix} \sigma-N+1, \sigma-N+\nu \\ \sigma-N+\nu+1 \end{matrix}; -p\right)$$

$$|\arg p| < \pi/2, \operatorname{R}(\sigma-N+1) > 0, \operatorname{R}(\sigma-N+\nu) > 0.$$

Using the relation  $E' u(t) = -E_{\nu-1}(t)$  we obtain, by integration by parts,

$$\int_0^t \left[ (\sigma+1) t^{\sigma} E_{\nu}(t^{n/s}) - \frac{n}{s} t^{\sigma+n/s} E_{\nu-1}(t^{n/s}) \right] dt = t^{\sigma+1} E_{\nu}(t^{n/s}).$$

Apply (R.7) and (6.5) with  $N=1$ , to get the image of left hand side. On simplifying (7, p. 209, 11) we get the image of right hand side in accordance with (5.4), thus verifying (6.5) with  $N=1$ .

(d) (i) The Hermite polynomial is defined (8, p. 369) by

$$He_N(x) = (-1)^N e^{\frac{1}{2}x^2} \cdot \frac{d^N}{dx^N} \left( e^{-\frac{1}{2}x^2} \right).$$

Using (5.2) in (R.11) we have, with  $\eta = -N$ ,

$$(6.8) \quad G \left[ t^N e^{-\frac{1}{2}t^2} He_N(t); \frac{\alpha_1, \dots, \alpha_m}{\eta_1, \dots, \eta_{m-1}}, -N, \rho \right] = \frac{(-1)^N \cdot 2^{\rho - \sum_i^m \alpha_i + N}}{\sqrt{\pi}} \cdot$$

multiplied by

$$G_{2m+2, 2m+1}^{1, 2m+2} \left( \frac{2}{t^2} \middle| \begin{array}{c} \frac{-\eta_1}{2}, \frac{-\eta_1+1}{2}, \dots, \frac{-\eta_{m-1}}{2}, \frac{-\eta_{m-1}+1}{2}, 0, \frac{1}{2}, \\ 0, \frac{-\eta_1-\alpha_1}{2}, \frac{-\eta_1-\alpha_1+1}{2}, \dots, \frac{-\eta_{m-1}-\alpha_{m-1}}{2}, \\ \dots, \frac{-\rho}{2}, \frac{-\rho+1}{2} \\ \dots, \frac{-\eta_{m-1}-\alpha_{m-1}+1}{2}, \frac{N-\alpha_m}{2}, \frac{N-\alpha_m+1}{2} \end{array} \right)$$

$R(p) > 0, R(\min \eta_j, \rho) > -1, j=1, 2, \dots, m-1; N$  is a positive integer.

with  $\alpha_j=0, j=1, 2, \dots, m-1; \alpha_m=\frac{1}{2}-m-k, N=-2m, \rho=0$  we have

$$W \left[ t^N e^{-\frac{1}{2}t^2} H_{2m}(t); k, m \right] = \frac{(-1)^N \cdot 2^{m+k} + N - \frac{1}{2}}{\sqrt{\pi}} \cdot$$

$$\times E \left\{ \frac{1}{4}(5-2k+2m), \frac{1}{4}(3-2k+m); \frac{p^2}{2} \right\}$$

$$R(p) > 0.$$

Further putting  $k = \frac{N+1}{2}$  we have,

$$t^N e^{-\frac{1}{2}t^2} H_{2m}(t) \doteq \frac{(-1)^N 2^N}{\sqrt{\pi}} E \left\{ \frac{1}{2}(2-N), \frac{1}{2}(1-N); \frac{p^2}{2} \right\}; R(p) > 0.$$

(ii) The Laguerre polynomial is defined (8, p. 369) by

$$L_N^\alpha(x) = \frac{e^x x^{-\alpha}}{N!} \cdot \frac{d^N}{dx^N} (e^{-x} \cdot x^{N+\alpha})$$

In (R.11) as  $\eta_1, \dots, \eta_m$  are symmetrical, replacing  $\eta_1$  (instead of  $\eta_m$ ) by  $\eta$  and using (5.3) in it, we obtain,

$$(6.9) G \left[ t^\nu e^{-t} \cdot L_N^{\nu+\eta}(t); \frac{\alpha_1, \dots, \alpha_m}{\eta, \eta_2, \dots, \eta_m, \rho} \right] \\ = \frac{p}{N} \times G_{m+1, m+1}^{m+1, 1} \left( p \mid \begin{matrix} \nu, \eta + \alpha_1, \eta_2 + \alpha_2, \dots, \eta_m + \alpha_m \\ \eta + N, \eta_2, \dots, \eta_m, \rho \end{matrix} \right)$$

$$|\arg p| < \pi/2, R(p+1) > 0, R(\eta_j + \nu) > -1, j=2, 3, \dots, m;$$

$$R(\eta + N + \nu + 1) > 0, R(\rho + \nu) > -1.$$

Putting  $\eta = 0$  and  $\alpha_j = 0, j = 1, 2, \dots, m-1; \alpha_m = \frac{1}{2} - m - k, \eta_m = 2m, \rho = 0$  we get a known result (15, p. 32). Also with  $\eta = 0$  and  $\alpha_j = 0, j = 1, 2, \dots, m; \rho = 0$  we get other known result (8, p. 175).

I am extremely thankful to Dr. B. R. Bhonsle for his help and guidance in the preparation of this paper. My thanks are also due to Principal V. H. Acharya for the facilities he gave to me.

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# POTASSIUM ADSORPTION RATIO OF SOME CROP-PLANTS IN SAND CULTURE

By

B. RAMA MOORTHY and K. V. PALIWAL

Division of Soil Science and Agricultural Chemistry, I. A. R. I., New Delhi

[ Received on 8th February, 1960 ]

The cation exchange capacity of the colloids and the potassium adsorption ratio of the equilibrium solutions are some of the soil-water-plant systems that are of importance in the mineral nutrition of plants with respect to Ca, Mg and K. Although the cation exchange capacity of soils was reported by Thomson and Way in 1850, that of plant-roots was reported only in 1916 by Devaux. That the differential cation exchange capacities of the soil and plant were involved in the differential uptake of the monovalent and divalent cations by plant roots was shown by Elgabaly and Wiklander (1949). Besides the exchange capacity, the degree of saturation of the colloid with respect to these ions is also important because it has been shown by Wiklander (1954) that the activity or the effective concentration of the simultaneously replaced ions are proportional to the activity of the adsorbed ions in the soil colloidal phase. Conversely also, the amounts of the ions adsorbed by the plant root-colloids from the displaced ions in the soil solution will be proportional to the activity of these ions in the soil solution modified by their activity coefficients (conversion factors used to convert gross concentration to effective concentration) in the plant-colloidal phase.

Woodruff (1955) has recently shown that the ratio of the activity of potassium  $a_K(s)$  to the square root of that of calcium  $\times a^{\frac{1}{2}} ca(s)$  in the soil solution in equilibrium with the soil is a measure of the potassium supplying power of the soil to the plant. This ratio has been termed the constant of the ratio law function by Taylor (1958), because the exchangeable phase of the colloid denoted by the subscript (ex) is completely characterised by this function as denoted by the following equation, derived by an application of the Donnan membrane equilibria:

$$\frac{a_K(s)}{a^{\frac{1}{2}} ca(s)} = \frac{a_K(ex)}{a^{\frac{1}{2}} ca(ex)}$$

The U. S. Salinity Laboratory (1954) treats Mg and Ca identically as may be justified from the first approximation to the formulae of Debye and Huckel for the activity coefficients of these ions in dilute solutions and takes the square root of their sum expressed in atoms in the denominator of this ratio law function. In this form it is called the potassium adsorption ratio abbreviated hereafter as K. A. R. of the solution.

Since the potassium supplying power of a soil to a plant depends on the difference in the potential of the ion in the two ends (the soil and the plant) taking the analogy

of a syphon of hydrostatics, it is necessary to take into account the potassium adsorption ratio of the plant as well as that of the soil as measured by their respective equilibrium solutions in order to account for the fact that the potassium supplying power of a soil depends not only upon itself but also the nature of the plant grown on it. The object of this investigation has been, therefore, set to measure the potassium adsorption ratio of a solution in equilibrium with the plants grown in said culture in the first instance since that is the K. A. R. of the plant itself.

#### METHODS AND MATERIALS

Plants grown from seeds of the following varieties were used for the purpose: *Zea mays* (maize) Kanpur type 41, *Phaseolus aureus* Roxb (Mung) Lucknow N. T., *Oryza sativa* L. (paddy) New Pusa-130, *Nicotiana tabacum* (Tobacco) Harrison special and *Triticum aestivum* (wheat) New Pusa-824. Seedlings of rice and tobacco were raised on the Delhi soil for transplanting them on the washed quartz sand of the sand culture, while the rest were raised directly in their sand cultures themselves. Five types of solutions designated  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$  and  $K_5$  were used, varying only in the concentrations of K and Ca for all the crops excepting paddy for which a different schedule including  $K_2$  was followed. The variations in K were by a factor of two forming a geometric progression while that of calcium were made so as to make the sum of these cations expressed in milli-equivalents the same in every solution as shown in Table I. The rest of the constituents were in one and the same concentration in all these types as those recommended by Hewitt (1952) for crop plants in general. The K and Ca of solution  $K_2$  only corresponds with those recommended by him. The last column of this table gives K. A. R. values of the various culture solutions used based on concentration instead of the activity of the ions in view of the very dilute nature of the solutions.

TABLE I.  
Levels of K and Ca in solutions used for  
sand culture\*

Designation of the solution	concentration in the solution		K. A. R. of the culture solution
	m.e./litre of K	m.e./litre of Ca	
$K_1$	4.00	6.00	$5.96 \times 10^{-2}$
$K_2$	2.00	8.00	2.70 ,
$K_3$	1.00	9.00	1.29 ,
$K_4$	0.50	9.50	0.63 ,
$K_5$	0.25	9.75	0.315 ,

\*The concentration of the rest of the nutrients was as follows in all the solutions.

$NO_3 = 10.0$ ;  $SO_4 = 3.024$ ;  $PO_4 = 4.0$ ;  $Mg = 3.0$ ;  $Na = 1.33$ ,  $Mn = 0.02$ ;  $Zn = 0.002$ ;  $Cu = 0.002$ ;  $B = 0.011$ ;  $Mo = 0.0002$ ;  $Fe^3 = 0.33$  (as citrate).

The solutions were changed completely once every week after rinsing, while the water losses were made up once every alternate day in winter and every day in summer using 50 to 300 cc. of the culture solution for the whole week depending upon the age and growth of the plant and the rest distilled water. Each level was replicated four times. The number of plants finally allowed after establishing themselves were 4 for 15 days from 2-5-1959 to 13-6-59 and 2 for 47 days from 29-5-1959 to 15-7-1959 of maize; 4 for 23 days from 29-3-59 to 21-4-59 and 2 for 53 days from 29-3-59 to 21-5-59 of mung; 6 for 77 days after transplanting from 1-8-1959 to 18-10-59 of rice; 2 for 77 days after transplanting from 31-12-1958 to 18-3-59 of tobacco; and 4 for 91 days from 29-9-1959 to 29-12-58 of wheat. They were then carefully removed from the sand in running tap water with their roots intact, washed thoroughly free of sand and solution with distilled water and then dried with filter paper before taking them up for determination of the potassium adsorption ratio of equilibrium solutions. The stage at which they were removed corresponded to the stage of flowering in all cases excepting wheat and mung which were removed on ear-emergence and seed ripening respectively so that the determinations refer to fully grown up plants.

The method used for the determination of K. A. R. of equilibrium solutions of plants which is thermodynamically equal to the K. A. R. of the colloids (in this case of the plants) as shown by Woodruff (1955) is similar to the one adopted by Taylor (1958) for the determination of the constant of the ratio law function of soils. This consisted of bringing the active material (in this case plants) into equilibrium with solutions prepared to have such a composition as to have initially various values for their K. A. R. and noting the change in this value which each solution undergoes as a result of equilibrium with the plant. The roots of the plants were dipped into the solutions, the quantities of which were taken in proportion to the fresh weight of plants to be put into it through a cut aperture and slit in the paper covering the mouth of the conical flask or beaker containing the solution and allowing 24 hours to reach equilibrium in diffused light in the laboratory maintained at about 23°C during summer months with a room cooler. This was taken as sufficient time to reach equilibrium on the basis of the report of Jenny (1953) that for a period of 10 to 20 hours barley roots rapidly accumulated ions not present in them in sufficient quantities from salt solutions and clay-suspensions. Much longer periods were avoided because of the fear of drastic changes in the metabolism of the plants. The roots were aerated by using them as means of mixing the solution with the water added to make up for the losses due to transpiration about every four hours during day and eight hours during night. Graphs were drawn connecting the change in the K. A. R. of the solution as a result of this treatment with the initial K. A. R. of the solution for the plants grown in each level of the culture solution used. From these graphs the initial K. A. R. of the solution which would undergo zero change in its K. A. R. on equilibrium with the plants is determined.

The determination of potassium was done by flamephotometer and of calcium and magnesium by titration with versenate as given in the U. S. Salinity Laboratory handbook (1954). The plants were then washed thoroughly with distilled water, the roots were then excised and dried in the oven at 70°C. The cation exchange capacity of dried roots were determined by the method of Schuffelen as adopted in this laboratory by Jain (1959). The ashes of the plant roots and tops were taken up for their contents of K, Ca and Mg after fusion with sodium carbonate.

TABLE II  
Variation in duplicate in reaching diffusion equilibrium with plants  
(conc. Expressed in Mols/litre  $\times 10^3$ )

Treat- ment No.	Pot No.	Fresh wt. of the Plant	Calcium		Magnesium		Potassium		KAR $\times 10^3$		Change in KAR $\times 10^3$	Mean in KAR $\times 10^3$	% deviation from the mean
			Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Diff.	Diff.			
K <sub>2</sub>	5B	18	1.515	1.07	0.515	0.50	0.3117	2.444	0.694	6.164	+5.47	3.8	
6A	18	-do-	1.125	-do-	0.50	-do-	2.3013	0.694	5.761	+5.067		5.27	
6B	19	1.64	1.13	0.515	0.47	0.0779	2.86	0.163	7.156	+6.988		4.3	
8A	26	-do-	1.01	-do-	0.55	-do-	3.068	0.168	7.772	+7.604		7.30	
K <sub>3</sub>	10A	18	1.515	0.71	-do-	0.43	0.3117	0.9205	0.694	2.672	+1.978	5.3	
10B	18	-do-	1.0	-do-	0.455	-do-	0.94	0.694	2.465	+1.771		1.87	
11A	18	1.64	0.80	-do-	0.49	0.0779	1.023	0.168	2.858	+2.69		3.8	
11B	17	-do-	1.32	-do-	0.55	-do-	1.139	0.168	3.077	+2.909		2.80	

N.B. 1. One plant was taken for Diffusion.

2. Solution taken for each plant is equal to three times its fresh wt.

TABLE III  
Potassium Adsorption Ratio of Maize at the age of 47 days  
(Conc. Expressed in Mols/litre  $\times 10^3$ )

Treat- ment of the Plants in gms.	Fresh wt.		Calcium		Magnesium		Potassium		KAR $\times 10^2$		Change in K.A.R. of the plant
	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	
$K_1$	300	1.515	1.185	0.515	0.41	0.3117	0.85	0.6947	2.153	+ 1.459	1.42
	435	1.64	0.55	0.515	0.28	0.0779	0.765	0.168	2.665	+ 2.497	
$K_2$	430	1.515	0.82	0.515	0.42	0.3117	0.710	0.694	2.016	+ 1.322	
	330	1.64	0.65	0.515	0.35	0.0779	0.738	0.168	2.333	+ 2.165	1.500
$K_3$	295	1.02	1.10	0.520	0.625	1.2467	0.670	3.194	1.612	- 1.582	
	230	1.515	0.75	0.515	0.46	0.3117	0.4575	0.694	1.342	+ 0.648	1.443
$K_4$	275	1.64	0.90	0.515	0.47	0.0779	0.483	0.168	1.306	+ 1.138	
	245	1.02	2.41	0.520	1.70	1.2467	0.692	3.194	1.075	- 2.119	
$K_5$	290	1.515	0.85	0.515	0.43	0.3117	0.401	0.694	1.121	+ 0.427	1.081
	243	1.64	0.58	0.515	0.36	0.0779	0.297	0.168	1.085	+ 0.917	
	190	1.02	1.775	0.520	0.60	1.2467	1.091	3.194	2.239	- 0.955	
	205	1.515	0.80	0.515	0.45	0.3117	0.3155	0.694	0.89	+ 0.196	1.12
	245	1.64	0.605	0.515	0.36	0.0779	0.176	0.168	0.578	+ 0.41	

N.B. 1. Two plants were taken for Diffusion.

2. Solution was taken two times the fresh wt. of the plants.

## RESULTS

The variation in the change of the K. A. R. of identical solutions when brought into "equilibrium" in plants of the same treatment in duplicate is shown in table II. This shows that this variation for the duplicates is 3.8, 4.3, 5.3 and 3.8% of their means. The likely error in these determinations may therefore be taken as something less than 6% when two plants are used instead of the single plants.

The analytical data of solutions used for this diffusion equilibration with maize harvested at the time of their flowering are shown in Table III. This shows that there are both  $\pm$  changes when the plants are put into the solutions used for diffusion indicating the existence of a value of the K. A. R. of the solution for which there will be no change on the introduction of the plants as shown in Fig. 1. Such

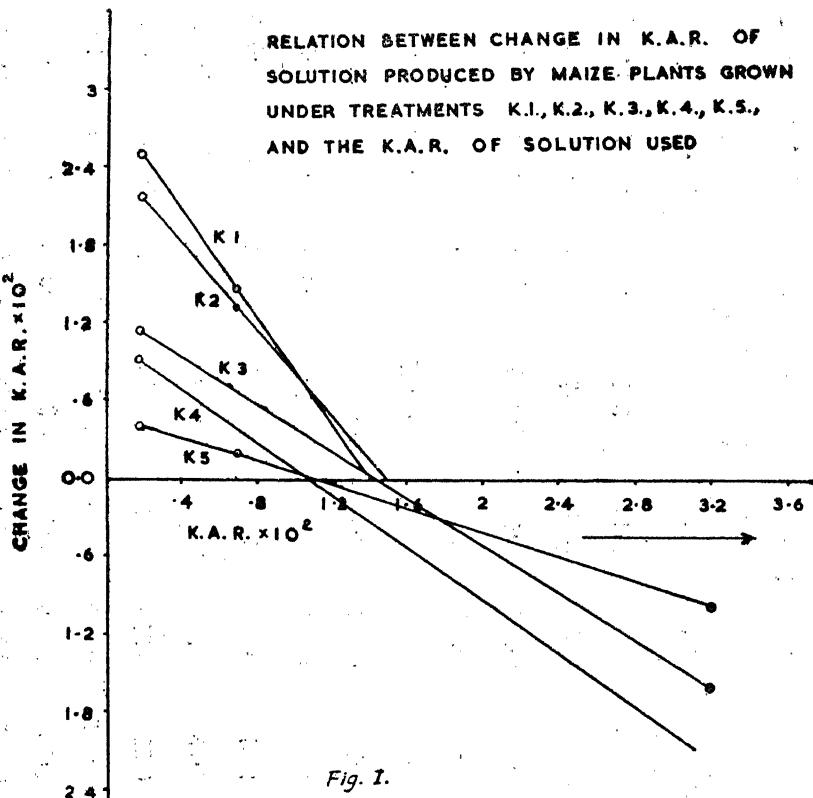


Fig. 1.

equilibrium K. A. R. of the solutions called the K. A. R. of the plant itself for the plants grown at different levels of the nutrients are shown in the last column. This shows that although the K. A. R. of the nutrient solutions K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub> used for the culture solutions varied from 5.96 to 1.29, the K. A. R. of the plants remained almost constant varying from 1.42 to 1.5 from the average value of 1.45. The KAR of the plants under treatments K<sub>4</sub> & K<sub>5</sub> was however different and was much lower with a value between 1.08 to 1.12. The plants were also abnormal under these two treatments with very thin stems and small leaves and their values may not therefore represent those of the normal healthy maize plants. Corresponding values for the batch of plants harvested earlier is shown in Table IV. This shows that the KAR

TABLE IV

Potassium Adsorption Ratio of Maize at the age of 15 days  
(Conc. Expressed in Mols/litre  $\times 10^3$ )

Treatment	Fresh wt. of the plants in gms.	Calcium		Magnesium		Potassium		KAR $\times 10^3$		Change in k. A. R. of the plant After K. A. R. Diff.
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	
K <sub>1</sub>	30.5	1.515	1.6	0.515	0.575	0.3117	0.7274	0.694	1.555	+0.861
K <sub>2</sub>	27.5	1.640	1.7	-do-	0.525	0.0779	0.896	0.163	1.89	+1.722
K <sub>3</sub>	20	1.515	1.55	-do-	0.55	0.3117	0.512	0.694	1.116	+0.422
K <sub>4</sub>	26	1.640	1.675	-do-	0.60	0.0779	1.024	0.163	2.147	+1.579
K <sub>5</sub>	17	1.515	1.575	-do-	0.575	0.3117	0.576	0.694	1.24	+0.546
K <sub>6</sub>	22	1.640	1.6	-do-	0.55	0.0779	0.768	0.163	1.657	+1.489
K <sub>7</sub>	18	1.515	1.75	-do-	0.60	0.3117	0.512	0.694	1.056	+0.362
K <sub>8</sub>	16	1.640	1.9	-do-	0.59	0.0779	0.64	0.168	1.28	+1.112
K <sub>9</sub>	18	1.515	1.3	-do-	0.55	0.3117	0.256	0.694	0.594	-0.10
K <sub>10</sub>	17	1.640	1.45	-do-	0.56	0.0779	0.259	0.168	0.578	+0.410
									0.588	

N.B. 1. Two plants were taken for Diffusions.

2. Solution was taken three times the fresh wt. of the plants.

TABLE V

**Potassium Adsorption Ratio of Mung**  
**(Conc. Expressed in Mols/litre  $\times 10^3$ )**

Treatment	Fresh wt. of the plants in gms.	Calcium		Magnesium		Potassium		KAR $\times 10^3$	Change in K. A. R. of the plant
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.		
$K_1$	34	1.515	1.60	0.515	0.550	0.3117	2.83	0.694	6.239 + 5.545
	21	1.640	0.95	0.515	0.405	0.0779	3.143	0.168	8.569 + 7.401
$K_2$	18	1.515	1.125	0.515	0.50	0.3117	2.301	0.694	5.761 + 5.067
	26	1.640	1.01	0.515	0.55	0.0779	3.068	0.168	7.772 + 7.604
$K_3$	18	1.515	0.71	0.515	0.48	0.3117	0.921	0.694	2.669 + 1.1975
	28	1.640	0.80	0.515	0.48	0.0779	1.023	0.168	2.858 + 2.69
$K_4$	32	1.515	0.95	0.515	0.46	0.3117	0.563	0.694	1.499 + 0.805
	42	1.640	0.89	0.515	0.50	0.0779	0.461	0.168	1.239 + 1.071
$K_5$	28	1.515	0.80	0.515	0.45	0.3117	0.614	0.694	1.748 + 1.054
	23	1.640	1.00	0.515	0.46	0.0779	0.588	0.168	1.537 + 1.369
									2.087

N.B. 1. Two plants were taken for Diffusion from treatment  $K_1$ ,  $K_4$  and  $K_5$  and one from  $K_2$  and  $K_3$ .

2. Solution was taken three times the fresh wt. of the plants.

TABLE VIIa

Potassium Adsorption Ratio of Wheat  
(Conc. Expressed in Mols/litre  $\times 10^3$ )

Treatment	Fresh wt. of the plants in gms.	Calcium		Magnesium		Potassium		KAR $\times 10^2$ Before Diff.	Change in K. A. R. of the plant
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.		
K <sub>4</sub>	77	0.70	0.975	0.55	0.625	0.48	0.201	1.36	0.503 -0.857
	73	0.975	1.325	0.55	0.65	0.1183	0.134	0.0702	0.301 0.269
	93	1.15	1.500	0.56	0.775	0.029	0.101	0.070	0.21 +0.140
	75	0.70	0.075	0.55	0.625	0.48	0.2568	1.36	0.663 -0.697
	79	0.975	1.10	0.55	0.625	0.1183	0.134	0.304	0.323 +0.019
K <sub>5</sub>	50	1.15	1.15	0.56	0.65	0.029	0.893	0.0702	0.211 +0.141

N. B. 1. Four plants were taken for the Diffusion.

2. Solution was taken three times the fresh wt. of the plants.

TABLE VIIb

Potassium Adsorption Ratio of Paddy  
(Conc. Expressed in Mols/litre  $\times 10^3$ )

Treatment	Fresh wt. of the plant	Ca + Mg.		K before Diff.		KAR $\times 10^2$ Before Diff.		Change in KAR $\times 10^2$ of Paddy
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	
K <sub>2</sub>	36	1.65	0.40	0.066	0.638	0.506	3.194	+2.688 0.7146
	30	1.90	0.25	0.033	0.760	0.231	3.406	+3.175

N. B. 1. One plant was taken for Diffusion.  
2. Solution was taken three times the fresh wt. of the plants.

TABLE VII  
Potassium Adsorption Ratio of Tobacco  
(Conc. Expressed in Mols/litre.  $\times 10^3$ )

Treatment	Fresh wt. of the plant in gms.	Calcium		Magnesium		Potassium		KAR $\times 10^3$		Change in K. A. R. of the plant.	
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.		
K <sub>1</sub>	200	1.802	0.375	0.616	0.575	0.374	1.4294	0.762	5.290	+4.528	
	206	1.970	0.35	0.616	0.60	0.0935	1.7864	0.183	7.300	+7.117	
K <sub>2</sub>	157	1.802	0.45	0.616	0.50	0.3750	0.893	0.762	2.899	+2.137	
	178	1.970	0.41	0.616	0.54	0.0935	1.105	0.183	3.586	+3.403	
K <sub>3</sub>	115	1.802	0.34	0.616	0.56	0.3740	0.826	0.762	2.757	+1.995	
	116	1.970	0.30	0.616	0.60	0.0935	0.670	0.183	2.235	+2.152	
K <sub>4</sub>	110	1.802	0.59	0.616	0.50	0.3740	0.737	0.762	2.131	+1.369	
	133	1.970	0.65	0.616	0.525	0.0935	0.625	0.183	1.821	+1.638	
K <sub>5</sub>	80	1.802	0.32	0.616	0.50	0.3740	0.491	0.762	1.739	+0.977	
	132	1.970	0.20	0.616	0.49	0.0935	0.383	0.183	1.461	+1.278	

N. B. 1. Two Plants were taken for diffusion.

2. Solution was taken two & half times the fresh weight of the plants.

\* Plants were stunted with particularly thick stems.

(\*) Thin stems with spotted chlorotic leaves.

at this early stage was lower and varied round about 1.14 to 0.84 neglecting the value for the last treatment for the reason already mentioned.

The analytical data connected with K. A. R. of the mung plants are presented in table V. Although the first two treatments seemed to show some stunting and one of the plants died in treatment K<sub>1</sub>, the variation in the K. A. R. of the plants under these five treatments is not much, changing only from 1.82 to 2.29 with an overall average value of 2.09, although more appropriately values of the plants under the K<sub>3</sub> and K<sub>4</sub> treatments could be taken as representative of the best plants in this series. The results for wheat and paddy are shown together in Table VI as the results for all the treatments are not available. This indicates that the K. A. R. of wheat is about 0.303 and of paddy 0.715.

Table VII shows the corresponding results for tobacco. It is seen from this that the K. A. R. of tobacco plants ranged from 2.77 to 3.05 with an average of 2.82 in the treatments that were free from stunted plants. Since the plants from the K<sub>5</sub> treatment showing some chlorosis were also in the above range of K. A. R. of the plants, the effect of changing widely the K. A. R. of the solutions and using higher concentrations in solutions used for diffusion equilibration on the K. A. R. of the plants has been studied. The results are presented in Table VIII for another set of plants harvested simultaneously with the previous set. This table shows that K. A. R. values falling in above noted range are obtained in the treatments K<sub>2</sub> and K<sub>3</sub> while the lower values are obtained in treatments showing chlorotic leaves. It appears therefore that the characteristics values of this constant are obtained only when the solutions used for diffusion equilibration as well as the nutrient solutions used for the growth of plants had both higher K or both lower K and not when one is low while the other is high.

TABLE VIII  
Potassium Adsorption Ratio of Tobacco  
(Conc. Expressed in Mols/litre  $\times 10^3$ )

Treatment	Fresh wt. of the plants in gms.	Calcium		Magnesium		Potassium		KAR $\times 10^3$		Change in K. A. R.	K. A. R. of the plant.
		Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.	Before Diff.	After Diff.		
K <sub>2</sub>	80	3.02	7.15	1.54	2.15	2.75	3.01	4.07	3.12	-0.95	2.94
	95	4.56	0.70	1.54	0.55	0.66	1.14	0.84	3.15	+2.31	
K <sub>3</sub>	130	3.02	6.55	1.54	3.43	2.75	2.68	4.07	2.68	-1.392	2.68
	68	4.56	2.30	1.54	0.48	0.66	1.54	0.84	2.90	+2.06	
K <sub>4</sub>	75	4.03	0.74	1.55	0.60	1.38	0.44	1.85	1.21	-0.63	1.46
	51	4.77	0.55	1.53	0.32	0.33	0.58	0.41	1.96	+1.55	1.45
K <sub>5</sub>	60	4.03	4.70	1.55	1.60	1.38	1.23	1.85	1.53	-0.32	1.39
	40	4.77	7.51	1.53	4.25	0.33	1.14	0.41	1.05	+0.63	

N. B. 1. One plant was taken for Diffusion.  
2. Solution was taken three times the fresh wt. of the Plant.

The C. E. C. of the plant roots are shown in table No. IX. This shows that plants with high K. A. R. have also generally high C. E. C. of roots with a co-efficient of correlation = + 0.947, seq. at 2 % level.

TABLE IX  
Cation exchange capacity of Plant roots.  
(Expressed in m.e./100 gms of Oven Dry Material.)

Treatment	Maize	Mung	Tobacco	Wheat	Paddy
K <sub>1</sub>	14.60	35.80	50.3	9.32	
K <sub>2</sub>	14.34	35.46	49.4	9.16	14.2
K <sub>3</sub>	14.56	35.44	49.6	9.18	
K <sub>4</sub>	14.36	35.52	49.4	9.27	
K <sub>5</sub>	14.64	35.28	49.3	9.07	
Average :	14.5	35.5	49.5	9.2	14.2
K. A. R. $\times 10^2$ :	1.45	2.09	2.82	0.308	0.715

#### DISCUSSION OF THE RESULTS

Arnon et al (1942) reported that plants lost metal cations to culture solutions at pH = 3 while Jacobson et al (1950) report appreciable losses of K from excised barley roots to HCl solutions below pH = 4.5. The latter have shown that these losses could be changed to accumulation by having a high KCl to HCl ratio in the solution indicating the existence of a reversible chemical reaction involving the exchange of K and H ions of the roots, presumably obeying Donnan membrane equilibrium conditions. The results of diffusion equilibrium for the healthy tobacco plants of the treatment K<sub>3</sub> tested intact in this investigation at two levels of concentration of the solutions (as given in table VII & VIII) gave the same ratio law constant for the plants and show that the Donnan membrane equilibrium is valid in these cases. However there seems to be two points which are not clear purely from the above physico-chemical concepts without assuming some sort of vital self-regulating mechanism in the plants. One is the near constancy of the K. A. R. of the plants grown under different treatments although limited to un-stunted plants and the other is the need for using concentrated levels of the nutrients in the solution used for diffusion equilibration in dealing with plants from higher level treatments and of relatively dilute levels of the former when dealing with these from lower level treatments. Further work is necessary to elucidate this regulating mechanism of the plants.

## SUMMARY

The potassium supplying power of a soil to a crop is thermodynamically a function of the difference in its Gibb's potential (or escaping tendency) in the soil and that in the plant. It has been shown by Woodruff (1955) that the soil portion of the potassium supplying power can be measured by taking the constant of the Donnan membrane function also known as the ratio law function in the form of the ratio of the activity or effective concentration of potassium in a solution in equilibrium with the soil to the square root of the activity of the major divalent ion like calcium in the solution. This may be generally speaking represented by the potassium adsorption ratio (K. A. R.) of the solution, being the same as the above excepting that the square root of the sum of calcium and magnesium activities is taken instead of calcium alone and is equal to a corresponding ratio in the colloidal or adsorbed phase in the soil. This investigation deals with the determination of the K. A. R. of plants grown in sand culture from the measurements in the corresponding equilibrium solution by the adoption of a method of Taylor (1958) for the determination of the constant of ratio law function of soils.

The potassium adsorption ratio of plants about the time of flowering was found to be  $2.82 \times 10^{-2}$  for tobacco,  $2.09 \times 10^{-2}$  for mung,  $1.45 \times 10^{-2}$  for maize  $0.715 \times 10^{-2}$  for paddy and  $0.308 \times 10^{-2}$  for wheat and varied generally with the cation exchange capacities of their roots which were 49.5, 35.5, 14.5, 14.2, and 9.2 m.e./100gms. of dry material respectively. The characteristic constant for the K. A. R. of the plant was independent of the K. A. R. of the nutrient culture solution used for treatments that showed no visible abnormality in the plants, or as the detailed work on tobacco showed only when plants grown in high K. A. R. of the culture solution were put in solutions of high K. A. R. used for equilibrating the plants for the determination of their K. A. R. and also when those from culture solutions of low values are put in equilibration solutions of low values. The K. A. R. of maize at the flowering stage was found to be higher than that at an early stage.

## ACKNOWLEDGMENTS

Our thanks are due to Dr. B. P. Pal, Director of Indian Agricultural Research Institute and the Institute Council for awarding a fellowship to one of us (K. V. P.) and enabling this work to be undertaken.

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## ERRATA

In figure 3 of the paper "On the Processing of Ilford G-5 Nuclear Emulsions for Distortionless Tracts" by A. P. Sharma published in the Proceedings, Section A, Vol 32, Part I of 1962, pp. 25-33, the points representing ordinate magnitudes for 0 and 600 values on abscissa scales do not represent the experimental points as shown. These points lie on the extrapolated curve.

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Published by Dr. R. K. Saksena, for the National Academy of Sciences, India, Allahabad  
and Printed by M. Sarwat Husain at The Mission Press, Allahabad

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